

TECH LIBRARY KAFB, NM
0344988

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE

No. 1653

CHARTS FOR THE COMPUTATION OF EQUILIBRIUM COMPOSITION
OF CHEMICAL REACTIONS
IN THE CARBON-HYDROGEN-OXYGEN-NITROGEN SYSTEM
AT TEMPERATURES FROM 2000° TO 5000° K

By Vearl N. Huff and Clyde S. Calvert

Flight Propulsion Research Laboratory
Cleveland, Ohio



Washington
July 1948

AFMDC
TECHNICAL LIBRARY
AFL 2811

6553/

8129

0 500000



NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE NO. 1653

CHARTS FOR THE COMPUTATION OF EQUILIBRIUM COMPOSITION OF CHEMICAL

REACTIONS IN THE CARBON-HYDROGEN-OXYGEN-NITROGEN SYSTEM

AT TEMPERATURES FROM 2000° TO 5000° K

By Vearl N. Huff and Clyde S. Calvert

SUMMARY

A rapidly convergent method is described for the calculation of the equilibrium composition of the carbon-hydrogen-oxygen-nitrogen system in the temperature range from 2000° to 5000° K. Charts are provided for the estimation and progressive adjustment of two independent variables on which the calculations are based. Additional charts are provided for the graphical calculation of the composition. The use of the method and the charts is illustrated by an example.

INTRODUCTION

The determination of the equilibrium composition of a chemical reaction is necessary for the solution of certain problems in chemistry and thermodynamics. When a reaction occurs at elevated temperatures, the products of reaction contain dissociated molecules which, when present in sufficient quantity, complicate the solution of the problem. The degree of dissociation is determined by the temperature of the products, their partial pressures, and an equilibrium constant for each dissociation reaction.

For reactions involving carbon, hydrogen, oxygen, and nitrogen at temperatures between 2000° and 5000° K and at pressures below 100 atmospheres, a direct solution of the equilibrium equations is impractical if not impossible. Accordingly, some method of successive approximation or trial and error is required.

If only two elements are present in the reaction the problem is less difficult. For example, a direct method for computing the equilibrium composition of the hydrogen-oxygen reaction is described in reference 1.

A method of computing the equilibrium composition of a mixture of the elements, carbon, hydrogen, oxygen, and nitrogen, by means of a method of successive approximation is given in reference 2. The method was applied to combustion in the cylinder of an internal-combustion engine. This method, although convenient for temperatures up to approximately 2000° to 2500° K, becomes cumbersome for temperatures at which a large fraction of the molecules are dissociated.

A somewhat similar method for the same elements is described and the results are applied to the combustion in a gun in reference 3. A compilation of thermal data required for equilibrium-composition calculations at temperatures up to 5000° K was given in this reference; a part of that data has been used in the preparation of the enclosed charts and has been reproduced as table I.

A procedure is presented for computing the equilibrium composition of a gas mixture corresponding to an assigned pressure and temperature that is especially convenient for the carbon-hydrogen-oxygen-nitrogen system in the temperature range from 2000° to 5000° K and for pressures from approximately $1/4$ to 100 atmospheres. Charts that guide in the process of successive approximation and aid in the details of the calculations are presented. The use of the method developed at the NACA Cleveland laboratory is illustrated by an example.

The products of reaction considered are gaseous water H_2O , hydrogen H_2 , hydroxyl radical OH , atomic hydrogen H , nitrogen N_2 , nitric oxide NO , atomic nitrogen N , carbon dioxide CO_2 , carbon monoxide CO , oxygen O_2 , and atomic oxygen O . For the temperatures, pressures, and chemical elements considered, the perfect gas laws were assumed and density correction for equilibrium constants was neglected.

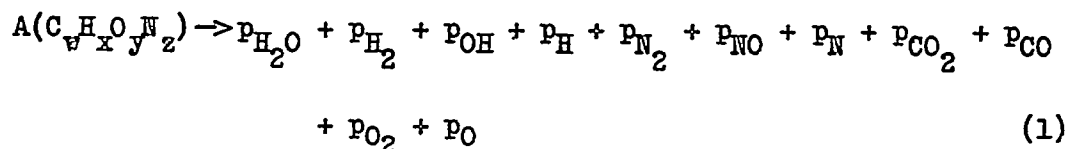
GENERAL SOLUTION

The procedure for determining the equilibrium composition of a chemical reaction at a selected temperature consists in assigning arbitrary values to two independent variables from which an exact equilibrium-composition total pressure and quantity of oxygen are computed. By a process of successive approximations, the values of the two independent variables are so adjusted that the calculated total pressure and quantity of oxygen approach the desired values.

Charts are presented that aid in the choice of the initial estimates and rapidly effect their adjustment. Additional charts are included that may be used to calculate the partial pressures of the products of reaction.

The compounds that are to react are represented by the equivalent formula $C_w H_x O_y N_z$ where w , x , y , and z are proportional to the total number of carbon, hydrogen, oxygen, and nitrogen atoms contained in the initial compounds. For convenience, the symbols are listed in appendix A.

The reaction under consideration can then be expressed in the following form:



where A is the number of formula weights of the equivalent formula $C_w H_x O_y N_z$ and the volume of the products of reaction V is numerically equal to the product of the gas constant and the temperature RT so that the total number of moles n of gaseous equilibrium products is numerically equal to the total pressure P . The partial pressure p_i of each gaseous product is similarly equal to the number of moles n_i of the product i , for example,
 $P_{H_2O} = n_{H_2O}$.

It is shown in appendix B that the partial pressure of each of the products can be computed when the value of the ratio of the partial pressure of water to the partial pressure of hydrogen, hereinafter designated the water-hydrogen ratio, $\Psi = P_{H_2O}/P_{H_2} = K_1 P_{CO_2}/P_{CO}$, and the value of A are known. The equilibrium constant K_1 is defined by equation (19), appendix B. The partial-pressure calculations can be arithmetically made by the use of equations given in appendix B, or if the required accuracy need not exceed 2 percent, the values may be found from the calculation charts shown in figure 1. The operations required for the use of figure 1 are discussed in a subsequent section where the details of its use are illustrated by an example.

In actual calculation, values of A and Ψ are initially estimated and a corresponding equilibrium composition is computed.

From the trial equilibrium composition, the corresponding total pressure P' and oxygen quantity Ay' are computed from the relations

$$P' = P_{H_2O} + P_{H_2} + P_{OH} + P_H + P_{N_2} + P_{NO} + P_N + P_{CO_2} + P_{CO} + P_{O_2} + P_O \quad (2)$$

and

$$Ay' = P_{H_2O} + P_{OH} + P_{NO} + 2P_{CO_2} + P_{CO} + 2P_{O_2} + P_O \quad (3)$$

where primes denote specific values of the variable resulting from trial calculations.

If the total pressure and the oxygen content resulting from a trial calculation are sufficiently close to the desired values, the problem is complete; otherwise the values of A and Ψ must be adjusted.

ESTIMATION AND ADJUSTMENT OF A AND Ψ

Estimation. - Instead of directly estimating A , estimation of the dissociation factor $A\Sigma/P_1$ is more expedient where

$$\Sigma = w + x/2 + z/2 \quad (4)$$

and

$$P_1 = P - p_{O_2} - p_O \quad (5)$$

The value of $A\Sigma/P_1$ is always between $1/2$ and 1 as shown in appendix B.

The oxygen ratio r is defined by the relation

$$r = \frac{2w + x/2}{y} \quad (6)$$

The quantity r is used to indicate mixture ratio and is the ratio of oxygen required for stoichiometric combustion to that supplied, therefore r is equal to 1 for a stoichiometric mixture and approaches zero as the proportion of oxygen is increased.

Values of Ψ and $A\Sigma/P_1$ are plotted in figure 2 as a function of r and temperature T for a pressure of 20.4 atmospheres for mixtures of oxygen with carbon, hydrogen, and hydrocarbon that has a hydrogen-carbon ratio x/w of 3. The effect of nitrogen on the values of Ψ and $A\Sigma/P_1$ is sufficiently small that it may be neglected in making the first estimates of Ψ and $A\Sigma/P_1$.

The desired values of r and Σ are computed from the specified values of w , x , y , and z . Values of Ψ and $A\Sigma/P_1$ are then estimated from the part of figure 2 that corresponds most closely to the x/w ratio of the reactant. (A considerable latitude in the choice of the initially estimated value of Ψ is permissible because the recommended process of adjustment rapidly corrects for initial errors.)

The partial pressures p_{O_2} and p_O are then computed by means of equations (36) and (37) or by the use of figure 1(a). By use of equation (5), P_1 is then computed and A is computed from the expression

$$A = (A\Sigma/P_1) P_1/\Sigma \quad (7)$$

Adjustment. - The initially estimated values of Ψ and $A\Sigma/P_1$ will, in general, require adjustment. At the end of a trial calculation, a more exact value for each quantity can be graphically obtained with aid of figure 2 or a similar plot.

The quantities $A\Sigma/P_1'$ and Ψ can be plotted on the appropriate part of figure 2 against the quantity r'

where

$$r' = \frac{A(2w + x/2)}{Ay'} \quad (8)$$

$$P_1' = P' - p_{O_2} - p_O \quad (9)$$

and the quantities P' and Ay' are computed from equations (2) and (3). A curve, similar to the existing curves, is drawn through the plotted points. New values of Ψ and $A\Sigma/P_1$ corresponding to the desired value of r are read from the newly sketched curve.

The process of obtaining and adjusting values for the estimated quantities is illustrated in the section **EXAMPLE OF EQUILIBRIUM-COMPOSITION CALCULATION**.

Properties of quantities Ψ and $A\Sigma/P_1$. - The values of Ψ and $A\Sigma/P_1$ for the three groups of reactants, carbon-, hydrogen-, and hydrocarbon-oxygen (hydrocarbon has an x/w ratio of 3), at a temperature of 3500° K and a pressure of 20.4 atmospheres are shown in figure 2(d).

For values of r less than 1.7, the value of Ψ is principally a function of r and to a first approximation is independent of Ψ and the x/w ratio. For values of r greater than 1.7, the value of Ψ and the shape of the Ψ -isotherm critically depend on the x/w ratio of the reactants.

The values of $A\Sigma/P_1$ and the shapes of the isotherms of $A\Sigma/P_1$ are nearly independent of the x/w ratio unless the proportion of carbon becomes large. For a reaction involving only carbon and oxygen, the quantity $A\Sigma/P_1$ always equals 1. The values of Ψ and $A\Sigma/P_1$ for other x/w ratios may be estimated by visual interpolation between figures 2(a), 2(b), and 2(c) or, if desired, approximate curves of Ψ and $A\Sigma/P_1$ may be computed for other hydrogen-carbon ratios by the method that is discussed in appendix B.

An asymptotic property of the quantity Ψ may be used to estimate Ψ and $A\Sigma/P_1$ for total pressures other than 20.4 atmospheres. As r is reduced (proportion of oxygen increased) the proportion of diatomic and monatomic oxygen in the products increases; at the limit of $r = 0$ only these species are present; hence

$$P = p_{O_2} + p_O \quad (10)$$

For a given value of temperature and pressure, Ψ can be determined from the relation

$$P = K_6 \Psi^2 + K_7 \Psi \quad (11)$$

This value of Ψ can be used to define a pseudo temperature T_p for which the pressure equals 20.4 atmospheres, that is

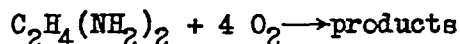
$$20.4 = K_{6,p} \Psi^2 + K_{7,p} \Psi \quad (12)$$

where $K_{6,p}$ and $K_{7,p}$ are the values of K_6 and K_7 , respectively, at the required pseudo temperature. Experience has shown that the pseudo temperature computed at $r = 0$ may be used for other values of r to obtain nearly correct initial estimates of both Ψ and $A\Sigma/P_1$ at pressures other than 20.4 atmospheres.

A plot of T_p against T for a range of pressures is shown in figure 3. In order to obtain estimates of Ψ and $A\Sigma/P_1$ at pressures other than 20.4 atmospheres, the value of T_p corresponding to the desired assigned temperature and pressure is found from figure 3. This T_p is used in figure 2 instead of T to obtain the first estimates of Ψ and $A\Sigma/P_1$.

EXAMPLE OF EQUILIBRIUM-COMPOSITION CALCULATION

The procedure used to compute equilibrium composition is illustrated by the calculation of the composition of the products of reaction of ethylenediamine ($C_2H_4(NH_2)_2$) and oxygen (O_2) at the stoichiometric ratio, a temperature of $4000^\circ K$, and a pressure of 10 atmospheres. The reaction is



By counting the number of atoms of each element in the equation, the following values of w , x , y , and z are obtained:

$$w = 2, x = 8, y = 8, z = 2$$

From these values and equation (6), the desired r is 1 (that is, the stoichiometric ratio):

$$r = \frac{2w + x/2}{y} = 1$$

and from equation (4), Σ is 7:

$$\Sigma = w + x/2 + z/2 = 7$$

For the assigned pressure of 10 atmospheres and the assigned temperature of 4000°K , a T_p of 4200°K is found from figure 3. For the desired r of 1 and a T_p of 4200°K , the initial estimates of Ψ and $A\Sigma/P_1$ are found from figure 2(c) to be 1.6 and 0.8, respectively. The estimated value of $A\Sigma/P_1$ is very close to the correct value; however, to illustrate the method of adjustment and the rapidity of its convergence, a value of $A\Sigma/P_1 = 0.84$ was deliberately chosen for the computation. In order to illustrate this example, an enlarged section of figure 2(c) has been reproduced as figure 4 and the points required for this problem are plotted.

From equations (36) and (37) of appendix B and the values of K_6 and K_7 in table I for 4000°K , the values of p_{O_2} and p_O corresponding to the estimated value of Ψ of 1.6 are found to be

$$\begin{aligned} p_{O_2} &= 0.8082 \\ p_O &= 1.3938 \end{aligned}$$

and by equations (5) and (7)

$$P_1 = P - p_{O_2} - p_O = 10 - 0.8082 - 1.3938 = 7.7980$$

and

$$A = (A\Sigma/P_1)(P_1/\Sigma) = \frac{(0.84)(7.798)}{7} = 0.9358$$

By the use of equations (39), (40), and (42) to (50) of appendix B and the equilibrium constants of table I corresponding to 4000°K the remaining partial pressures are found to be:

$$\begin{aligned} p_{H_2} &= 0.8782 & p_{N_2} &= 0.7907 & p_{CO_2} &= 0.2893 \\ p_{OH} &= 1.4236 & p_{NO} &= 0.2409 & p_{CO} &= 1.5823 \\ p_H &= 1.4965 & p_N &= 0.0493 & & \\ p_{H_2O} &= 1.4051 & & & & \end{aligned}$$

From these partial pressures and equations (8), (2), and (9), the values of r' , P' , and $A\Sigma/P_1'$ corresponding to the estimated values of A and Ψ are found to be

$$\begin{aligned} r' &= \frac{A(2w + x/2)}{Ay'} \\ &= 0.9085 \end{aligned}$$

where

$$\begin{aligned} Ay' &= p_{H_2O} + p_{OH} + p_{NO} + 2p_{CO_2} + p_{CO} + 2p_{O_2} + p_O \\ &= 8.2407 \end{aligned}$$

and

$$\begin{aligned} P' &= p_{H_2O} + p_{H_2} + p_{OH} + p_H + p_{N_2} + p_{NO} + p_N + p_{CO_2} + p_{CO} + p_{O_2} + p_O \\ &= 10.3579 \text{ atmospheres} \end{aligned}$$

$$\begin{aligned} P_1' &= 10.3579 - 0.8082 - 1.3938 \\ &= 8.1559 \end{aligned}$$

therefore

$$\begin{aligned} A\Sigma/P_1' &= \frac{(0.9358)(7)}{8.1559} \\ &= 0.8032 \end{aligned}$$

If the values of r' and P' do not agree closely enough with the desired values, the quantities Ψ and A must be reestimated. The values of Ψ and $A\Sigma/P_1'$ can be plotted in figure 2(c) against r' and are again shown in figure 4. Segments of curves similar in shape to the existing curves are sketched through the plotted points; new values for Ψ of 1.4 and for $A\Sigma/P_1'$ of 0.81 are read from the newly sketched curves at $r = 1$ (the desired value).

The second trial calculation is based upon the newly estimated values of Ψ and $A\Sigma/P_1$ with the result that

$$p_{O_2} = 0.6188 \quad p_{H_2} = 0.9728 \quad p_{N_2} = 0.8127 \quad p_{CO_2} = 0.2605$$

$$p_O = 1.2195 \quad p_{OH} = 1.3111 \quad p_{NO} = 0.2137 \quad p_{CO} = 1.6283$$

$$p_1 = 8.1617 \quad p_H = 1.5751 \quad p_N = 0.0500$$

$$A = 0.9444$$

whereby

$$r' = 1.0083$$

$$P' = 10.0244 \text{ atmospheres}$$

$$A\Sigma/P_1' = 0.8076$$

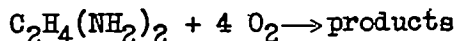
These values are in close agreement with the desired values of r and P .

The detailed calculations and the results of this example are shown in table II.

GRAPHICAL CALCULATION OF PARTIAL PRESSURES

The numerical calculation of partial pressures involves tedious and time-consuming operations that include reference to tables of equilibrium constants. As an aid to the computation, the solutions of the equilibrium equations have been plotted in figure 1.

The procedure required to obtain the partial pressure of each of the products of reaction from the charts is illustrated for the preceding example by the guide lines shown on each part of figure 1. The conditions for the example are



$$w = 2, x = 8, y = 8, z = 2$$

$$r = 1, \Sigma = 7, P = 10 \text{ atmospheres, } T = 4000^\circ \text{ K}$$

As in the preceding example, the first estimates of Ψ and $A\Sigma/P_1$ are 1.6 and 0.84, respectively.

The partial pressures p_{O_2} and p_O are plotted against Ψ in figure 1(a) for various temperatures. For $\Psi = 1.6$ and $T = 4000^\circ \text{K}$, $p_{O_2} = 0.81$ and $p_O = 1.39$.

Whereby

$$P_1 = 10 - 0.81 - 1.39 = 7.80$$

$$A = 0.84 \frac{7.800}{7} = 0.936$$

$$\frac{Ax}{\Psi+1} = \frac{(0.936)(8)}{1.6+1} = 2.88$$

$$Az = (0.936)(2) = 1.872$$

$$Aw = (0.936)(2) = 1.872$$

A plot of Ψ against a , which is defined by equation (39), for various temperatures and a plot of p_{H_2} against a for various values of $Ax/\Psi+1$ are given in figure 1(b). For $\Psi = 1.6$ and $T = 4000^\circ \text{K}$, $a = 1.20$; for $a = 1.20$ and $Ax/\Psi+1 = 2.88$, $p_{H_2} = 0.88$.

Figure 1(c) is composed of two parts. The constant temperature lines in the upper left section are plots of p_H against p_{H_2} for various temperatures. For $p_{H_2} = 0.88$ and $T = 4000^\circ \text{K}$ (read from the scale marked temperature T for atomic hydrogen H), $p_H = 1.50$. By the use of a set of reference lines that correspond to constant values of $\Psi \sqrt{p_{H_2}}$ and the second set of constant temperature lines (in the lower right section) p_{OH} is computed. For $\Psi = 1.6$ and $p_{H_2} = 0.88$, the reference line q is found. At the intersection of q and the temperature line $T = 4000^\circ \text{K}$ (read from the scale marked temperature T for hydroxyl radical OH), $p_{OH} = 1.42$.

A plot of Ψ against b , which is defined by equation (42), for various temperatures and a plot of p_{N_2} against b for various values of Az are shown in figure 1(d). When $\Psi = 1.6$ and $T = 4000^\circ \text{K}$, $b = 0.326$. For $b = 0.326$ and $Az = 1.872$, $p_{N_2} = 0.79$.

The constant temperature lines in the upper left section of figure 1(e), which is composed of two parts, are plots of p_N against p_{N_2} for various temperatures. For $p_{N_2} = 0.79$ and $T = 4000^\circ \text{K}$ (read from the scale marked temperature T for atomic nitrogen N), $p_N = 0.049$. By the use of a set of reference lines that correspond to constant values of $\Psi \sqrt{p_{N_2}}$ and a second set of constant temperature lines (in the lower right section) p_{NO} is computed. For $\Psi = 1.6$ and $p_{N_2} = 0.79$, the reference line q is found. At the intersection of q and the temperature line $T = 4000^\circ \text{K}$ (read from the scale marked temperature T for nitric oxide NO), $p_{NO} = 0.241$.

A plot of p_{CO_2}/p_{CO} against Ψ for various temperatures and plots of p_{CO_2} against p_{CO_2}/p_{CO} for various values of A_w when $p_{CO_2}/p_{CO} \leq 1$ and p_{CO} plotted against p_{CO_2}/p_{CO} for various values of A_w when $p_{CO_2}/p_{CO} \geq 1$ is presented in figure 1(f). This chart is so constructed that only the smaller of the two quantities p_{CO_2} or p_{CO} is determined. The larger of either of these quantities is obtained by subtraction from A_w . For $\Psi = 1.6$ and $T = 4000^\circ \text{K}$, $p_{CO_2}/p_{CO} = 0.183$ and for $A_w = 1.872$, $p_{CO_2} = 0.290$ and $p_{CO} = 1.872 - 0.290 = 1.582$.

The quantity p_{H_2O} is equal to Ψ times p_{H_2} ; therefore $p_{H_2O} = (1.6)(0.88) = 1.408$. From these values of partial pressures, $A_y' = 8.241$, $r' = 0.9086$, and $P_1' = 10.360$.

New estimation of Ψ and A are obtained as previously explained and a second trial calculation is made if the values of P' and r' are to be brought closer to the desired values of 10 and 1, respectively. The results of two trial calculations made by the graphical method have been tabulated in table II.

Numerical checks on calculations. - A check on the accuracy of the chart calculations can be made by substituting the partial pressures obtained from a trial calculation in equations (32) and (34) to determine A_x and A_z . The values obtained for this example are

$$Ax = (2)(1.408) + (2)(0.88) + 1.42 + 1.50 = 7.496$$

$$Az = (2)(0.79) + 0.241 + 0.049 = 1.870$$

These values are to be compared with $Ax = (0.936)(8) = 7.488$ and $Az = 1.872$.

When the values Ax and Az do not check exactly, improvement of the accuracy of the calculations is possible by use of equations for the mass balance.

If, as will usually be the case, the sum of p_{OH} and p_H is less than $\frac{1}{2}Ax$ and the sum of p_{NO} and p_N is less than $\frac{1}{2}Az$, the following equations can be used to compute better values for p_{N_2} , p_{H_2} , and p_{H_2O}

$$\begin{aligned} p_{N_2}' &= \frac{Az - p_{NO} - p_N}{2} & (13) \\ &= \frac{1.872 - 0.241 - 0.049}{2} \\ &= 0.791 \end{aligned}$$

when $p_{H_2O} > p_{H_2}$

$$\begin{aligned} p_{H_2}' &= \frac{Ax - p_{OH} - p_H}{2(\Psi + 1)} & (14) \\ &= \frac{7.488 - 1.42 - 1.50}{(2)(1.6) + 1} \\ &= 0.878 \end{aligned}$$

$$\begin{aligned} p_{H_2O}' &= \frac{Ax - p_{OH} - p_H}{2} - p_{H_2} & (15) \\ &= \frac{7.488 - 1.42 - 1.50}{2} - 0.878 \\ &= 1.406 \end{aligned}$$

and when $p_{H_2O} < p_{H_2}$

$$p_{H_2O}' = \frac{Ax - p_{OH} - p_H}{2(\Psi + 1)} \Psi \quad (16)$$

$$p_{H_2}' = \frac{Ax - p_{OH} - p_H}{2} - p_{H_2O} \quad (17)$$

Flight Propulsion Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, April 1, 1948.

APPENDIX A

SYMBOLS

A	number of formula weights of the equivalent formula $C_w H_x O_y N_z$
$\Delta \Sigma / P_1$	dissociation factor, moles/atm
a	$\frac{K_9 + \Psi K_{10}}{\Psi + 1}$ term of quadratic equation
b	$K_8 + \Psi K_3$ term of quadratic equation
$C_w H_x O_y N_z$	equivalent formula for compounds that are to react
K_1, K_3, \dots	equilibrium constants
n	total number of moles of products of reaction
n_{H_2O}, n_{H_2}, \dots	number of moles of water, hydrogen, . . . , respectively
P	total pressure of products of reaction
P_1	$P - p_{O_2} - p_O$
p_{H_2O}, p_{H_2}, \dots	partial pressure of water, hydrogen, . . . , respectively
R	gas constant, 1.987, cal/(mole)(°K)
r	oxygen ratio, $\frac{2w + x/2}{y}$
T	temperature, °K
T_p	pseudo temperature, °K
V	volume of products of reaction, cal/atm
v, w, x, y, z	total number of atoms of lithium, carbon, hydrogen, oxygen, and nitrogen, respectively, in initial compounds.

$$\Sigma \quad w + x/2 + z/2$$

$$\Psi \quad \text{water-hydrogen ratio, } p_{\text{H}_2\text{O}}/p_{\text{H}_2}$$

Primes are used to indicate specific values of the variable resulting from trial calculations.

APPENDIX B

DERIVATION OF EQUATIONS

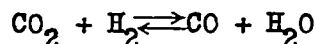
In this section it is shown how the equations for the conservation of mass and the equilibrium equations are combined to form the working equations required for the computation of an equilibrium composition. The range for the quantity $A\Sigma/P_1$ and expressions used for plotting approximate and exact hydrocarbon curves, similar to those of figure 2, are shown.

Basic Equations

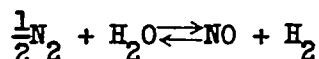
By definition

$$\Psi = \frac{P_{H_2O}}{P_{H_2}} \quad (18)$$

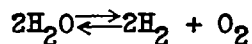
The following dissociation reactions and the corresponding equilibrium equations were considered for the derivation. These equations together with the values of the equilibrium constants were taken from reference 3.



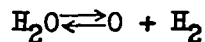
$$K_1 = \frac{P_{CO}}{P_{CO_2}} \Psi \quad (19)$$



$$K_3 = \frac{P_{NO}}{\Psi \sqrt{P_{N_2}}} \quad (20)$$



$$K_6 = \frac{P_{O_2}}{\Psi^2} \quad (21)$$



$$K_7 = \frac{P_O}{\Psi} \quad (22)$$

$$\frac{1}{2}\text{N}_2 \rightleftharpoons \text{N}$$

$$K_8 = \frac{p_{\text{N}}}{\sqrt{p_{\text{N}_2}}} \quad (23)$$

$$\frac{1}{2}\text{H}_2 \rightleftharpoons \text{H}$$

$$K_9 = \frac{p_{\text{H}}}{\sqrt{p_{\text{H}_2}}} \quad (24)$$

$$\text{H}_2\text{O} \rightleftharpoons \frac{1}{2}\text{H}_2 + \text{OH}$$

$$K_{10} = \frac{p_{\text{OH}}}{\Psi \sqrt{p_{\text{H}_2}}} \quad (25)$$

The law of conservation of mass yields the following equations:

$$A(\text{C}_w\text{H}_x\text{O}_y\text{N}_z) \rightarrow n_{\text{H}_2\text{O}} + n_{\text{H}_2} + n_{\text{OH}} + n_{\text{H}} + n_{\text{N}_2} + n_{\text{NO}} + n_{\text{N}} + n_{\text{CO}_2} + n_{\text{CO}} \\ + n_{\text{O}_2} + n_{\text{O}} \quad (26)$$

$$Ax = 2n_{\text{H}_2\text{O}} + 2n_{\text{H}_2} + n_{\text{OH}} + n_{\text{H}} \quad (27)$$

$$Ay = n_{\text{H}_2\text{O}} + n_{\text{OH}} + n_{\text{NO}} + 2n_{\text{CO}_2} + n_{\text{CO}} + 2n_{\text{O}_2} + n_{\text{O}} \quad (28)$$

$$Az = 2n_{\text{N}_2} + n_{\text{NO}} + n_{\text{N}} \quad (29)$$

$$Aw = n_{\text{CO}_2} + n_{\text{CO}} \quad (30)$$

Equations (18) to (25) are in terms of partial pressures whereas equations (26) to (30) are in terms of moles. When a volume is so chosen for the reaction that

$$\frac{RT}{V} = 1$$

and the perfect-gas law is assumed, that is

$$PV = nRT$$

$$\frac{P}{n} = \frac{RT}{V} = 1 \quad (31)$$

and

$$P = n$$

Similarly

$$p_{H_2O} = n_{H_2O}$$

therefore equations (27) to (30) may be written

$$Ax = 2p_{H_2O} + 2p_{H_2} + p_{OH} + p_H \quad (32)$$

$$Ay = p_{H_2O} + p_{OH} + p_{NO} + 2p_{CO_2} + p_{CO} + 2p_{O_2} + p_O \quad (33)$$

$$Az = 2p_{N_2} + p_{NO} + p_N \quad (34)$$

$$Aw = p_{CO_2} + p_{CO} \quad (35)$$

Working Equations

The equations shown in the preceding section are combined to form the relations used for calculating the partial pressures. The quantities p_{O_2} and p_O are obtained from equations (21) and (22).

$$p_{O_2} = \Psi^2 K_6 \quad (36)$$

$$p_O = \Psi K_7 \quad (37)$$

Equations (18), (24), (25), and (32) are combined to form the following quadratic equation for p_{H_2} in terms of Ψ , K_9 , K_{10} , and A :

$$2p_{H_2} + \frac{K_9 + \Psi K_{10}}{\Psi + 1} \sqrt{p_{H_2}} - \frac{Ax}{\Psi + 1} = 0 \quad (38)$$

if

$$a = \frac{K_9 + \Psi K_{10}}{\Psi + 1} \quad (39)$$

$$p_{H_2} = \frac{1}{16} \left(-a + \sqrt{a^2 + \frac{8Ax}{\Psi + 1}} \right)^2 \quad (40)$$

Equations (20), (23), and (34) are combined to form the following quadratic equation for p_{N_2} in terms of Ψ , K_3 , K_8 , and A

$$2p_{N_2} + (K_8 + \Psi K_3) \sqrt{p_{N_2}} - Az = 0 \quad (41)$$

if

$$b = K_8 + \Psi K_3 \quad (42)$$

$$p_{N_2} = \frac{1}{16} \left(-b + \sqrt{b^2 + 8Az} \right)^2 \quad (43)$$

For given values of x , z , and temperature, and by estimating values for A and Ψ , p_{H_2} and p_{N_2} can be computed.

The remaining partial pressures can then be computed. Equations (18), (20), and (23) to (25) are rewritten:

$$p_{H_2O} = \Psi p_{H_2} \quad (44)$$

$$p_{OH} = \Psi K_{10} \sqrt{p_{H_2}} \quad (45)$$

$$p_H = K_9 \sqrt{p_{H_2}} \quad (46)$$

$$p_{NO} = \Psi K_3 \sqrt{p_{N_2}} \quad (47)$$

$$p_N = K_8 \sqrt{p_{N_2}} \quad (48)$$

By combining equations (19) and (35)

$$p_{CO_2} = \frac{Aw}{1 + \frac{K_1}{\Psi}} \quad (49)$$

$$p_{CO} = Aw - p_{CO_2} \quad (50)$$

or

$$p_{CO} = \frac{Aw}{1 + \frac{\Psi}{K_1}} \quad (49a)$$

$$p_{CO_2} = Aw - p_{CO} \quad (50a)$$

Range of Values of $A\Sigma/P_1$

From equations (2) and (5)

$$P_1 = p_{H_2O} + p_{H_2} + p_{OH} + p_H + p_{N_2} + p_{NO} + p_N + p_{CO_2} + p_{CO} \quad (51)$$

and from equations (4), (32), (34), and (35)

$$\begin{aligned} A\Sigma &= Aw + Ax/2 + Az/2 \\ &= p_{CO_2} + p_{CO} + p_{H_2O} + p_{H_2} + \frac{p_{OH} + p_H}{2} + p_{N_2} + \frac{p_{NO} + p_N}{2} \end{aligned} \quad (52)$$

By division of equation (52) by (51) and by simplification

$$A\Sigma/P_1 = 1 - \frac{p_{OH} + p_H + p_{NO} + p_N}{2P_1} \quad (53)$$

The maximum value of $A\Sigma/P_1$ occurs where $p_{OH} + p_H + p_{NO} + p_N = 0$ and the minimum value occurs when $p_{OH} + p_H + p_{NO} + p_N = P_1$; hence

$$1 \geq A\Sigma/P_1 \geq \frac{1}{2}$$

$A\Sigma/P_1$ is a dissociation factor, the value of which is less than 1 when molecules containing one atom of hydrogen or nitrogen are present. This factor is used to estimate A .

Approximate Interpolation Formulas for Hydrocarbon-Oxygen Reactions

Approximate curves of Ψ and $A\Sigma/P_1$ as a function of r can be constructed for any hydrocarbon-oxygen reaction by the following method:

For a given value of Ψ and temperature, r_C and r_H are read from figures 2(a) and 2(b), respectively, and $(A\Sigma/P_1)_H$ is read from figure 2(b) at r_H . Values of r_{CH} and $(A\Sigma/P_1)_{CH}$ for the hydrocarbon are computed from the approximate equations.

$$r_{CH} = \frac{\frac{2w}{r_C} + \frac{x}{2}}{\frac{2w}{r_C} + \frac{x}{2r_H}} \quad (54)$$

$$\left(\frac{A\Sigma}{P_1}\right)_{CH} = 1 - \left[1 - \left(\frac{A\Sigma}{P_1}\right)_H\right] \sqrt{\frac{x}{2w + x}} \quad (55)$$

The quantities Ψ and $(A\Sigma/P_1)_{CH}$ are plotted against r_{CH} to form a family of curves similar to those of figure 2(c).

Equations (54) and (55) are exact for the limiting case of low temperature and high pressure when p_{OH} and p_H are equal to zero; equation (54) is exact for the limiting case of high temperature and low pressure when p_{H_2O} and p_{H_2} are equal to zero.

Except for special cases, small errors exist in both equations (54) and (55). The order of magnitude of these errors is indicated in the following table for $T = 4000^\circ \text{K}$, and $P = 20.4$ atmospheres.

x/w	Ψ	r_{CH}		Error (percent)
		Exact value	Approximate value	
1	0.1	2.3425	2.3454	0.12
1	.3	2.1103	2.1183	.38
1	.4	.6499	.6718	3.37
4	.1	3.2848	3.2893	.14
$(A\Sigma/P_1)_{CH}$				
1	0.1	0.91584	0.91352	0.25
1	.3	.91396	.91152	.27
1	.4	.86366	.85657	.82
4	.1	.87814	.87770	.05

Exact Equations for Plotting Hydrocarbon Curves.

The following exact equations may be used to construct plots of $A\Sigma/P_1$ and Ψ against r similar to those in figure 2(c) for the carbon-hydrogen-oxygen system:

$$r_{CH} = \frac{2w + x/2}{w \left(\frac{2\Psi + K_1}{\Psi + K_1} \right) + \frac{x\Psi}{(\Psi + 1)(2\sqrt{P_{H_2}} + a)} \left(\sqrt{P_{H_2}} + K_{10} + \frac{2\Psi K_6 + K_7}{\sqrt{P_{H_2}}} \right)} \quad (56)$$

$$\left(\frac{A\Sigma}{P_1} \right)_{CH} = 1 - \frac{a \sqrt{P_{H_2}} (\Psi + 1)}{2P_1} \quad (57)$$

where

$$\sqrt{P_{H_2}} = -\frac{a}{2} \left(\frac{w + x}{2w + x} \right) \sqrt{\left[\frac{a}{2} \left(\frac{w + x}{2w + x} \right) \right]^2 + \frac{P_1 x}{(\Psi + 1)(2w + x)}} \quad (58)$$

$$a = \frac{K_9 + \Psi K_{10}}{\Psi + 1} \quad (39)$$

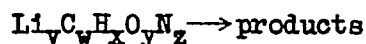
Equation (58) may be used to simplify the calculation of equilibrium compositions in the carbon-hydrogen-oxygen system. When equation (58) is used, the total pressure is always exact and it is therefore unnecessary to estimate $A\Sigma/P_1$; only Ψ need be estimated.

APPENDIX C

CALCULATION OF EQUILIBRIUM COMPOSITION WITH ELEMENTS IN

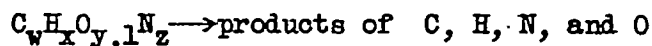
ADDITION TO CARBON, HYDROGEN, OXYGEN, AND NITROGEN

The method presented for the solution of the carbon-hydrogen-oxygen-nitrogen system often can be used to aid in the solution of problems involving other elements by dividing the reaction into two parts. For example, if lithium Li is added to the carbon-hydrogen-oxygen-nitrogen mixture, the reaction can be expressed by the equation

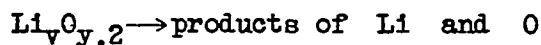


where v is the number of atoms of lithium.

Let the first part of the reaction be



and the second part will be

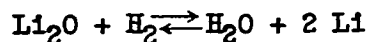


In order to make this division of the problem, the following requirements must be met:

1. The pressure of p_{O_2} and p_0 must be the same in both parts of the reaction and must be considered only once in the computation of the total quantity of oxygen or the total pressure.
2. The formation of compounds other than oxides must be considered and, if present, they must be correctly accounted for (for example, LiH).

The products of the first part of the reaction can be found by means of figure 1 and the products of the second part are determined by some other method.

If it may be assumed that no reaction except the formation of the oxide is present, the method becomes fairly easy. An example is subsequently presented to illustrate the procedure for calculation. For this purpose, a dissociation reaction has arbitrarily been assigned:

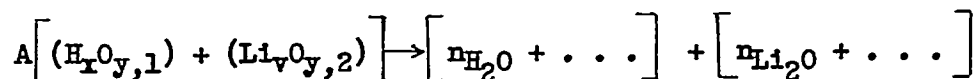


the dissociation constant has been assigned an arbitrary value because no data are available, therefore

$$K = \frac{p_{\text{H}_2\text{O}} p_{\text{Li}}^2}{p_{\text{H}_2} p_{\text{Li}_2\text{O}}} = 0.1 \quad (59)$$

by assumption for a temperature of 4400°K . All compounds and elements are assumed to be gases. These assumptions probably are not valid for the lithium reaction and should not be used for any purpose other than illustration.

Let the desired reaction be:



for

$$v = 2, x = 4, y = 3, T = 4400^\circ \text{K}, P = 20.4 \text{ atmospheres}$$

Because $P = n$

$$2p_{\text{Li}_2\text{O}} + p_{\text{Li}} = Av \quad (60)$$

When equations (18), (59), and (60) are combined

$$\frac{1}{2} p_{\text{Li}}^2 + \frac{K}{4\psi} p_{\text{Li}} - \frac{AvK}{4\psi} = 0 \quad (61)$$

let

$$c = \frac{K}{4\psi} \quad (62)$$

and

$$p_{\text{Li}} = -c + \sqrt{c^2 + \frac{Avk}{2\psi}} \quad (63)$$

$$p_{Li_2O} = \frac{Av - p_{Li}}{2} \quad (64)$$

For this reaction r would be expressed

$$\begin{aligned} r &= \frac{v + x}{2y} \\ &= \frac{2 + 4}{6} \\ &= 1 \end{aligned}$$

and Σ would be

$$\Sigma = v/2 + x/2 = 2/2 + 4/2 = 3$$

where $v/2$ appears because two atoms of Li are required to form the normal oxide Li_2O . In the absence of a plot of Ψ and $A\Sigma/P_1$ for lithium, hydrogen, and oxygen, figure 2(b) may be used from which

$$\Psi = 0.87 \text{ and } A\Sigma/P_1 = 0.715$$

and from figure 1(a)

$$p_{O_2} = 0.96$$

$$p_O = 3.05$$

whence

$$P_1 = 20.4 - 0.96 - 3.05 = 16.39$$

$$A = (A\Sigma/P_1) p_1/\Sigma = 0.715 \frac{16.39}{3} = 3.91$$

$$Ax/(\Psi + 1) = \frac{(3.91)(4)}{1.87} = 8.36$$

From figure 1

$$p_{H_2} = 2.25$$

$$p_{H_2O} = (2.25)(0.87) = 1.96$$

$$p_{OH} = 2.72$$

$$p_H = 4.51$$

From equation (62)

$$c = \frac{0.1}{(4)(0.87)} = 0.0287$$

and

$$\frac{AvK}{2\Psi} = \frac{(3.91)(2)(0.1)}{(2)(0.87)} = 0.449$$

and from equation (63)

$$p_{Li} = -0.0287 + \sqrt{(0.0287)^2 + 0.449} = 0.642$$

From equation (64)

$$p_{Li_2O} = \frac{(3.91)(2) - 0.642}{2} = 3.59$$

$$p_1 = 2.25 + 1.96 + 2.72 + 4.51 + 0.64 + 3.59 = 15.67$$

$$P = p_1 + 0.96 + 3.05 = 19.68$$

$$Ay = (2)(0.96) + 3.05 + 1.96 + 2.72 + 3.59 = 13.24$$

$$r = \frac{A(v+x)}{2Ay} = \frac{(3.91)(6)}{(2)(13.24)} = 0.886$$

$$A\Sigma/P_1 = \frac{(3.91)(3)}{15.67} = 0.749$$

The composition thus obtained is correct for a pressure of 19.68 atmospheres and for an oxygen ratio of 0.886. A closer approximation to

the desired values of $r = 1$ and $P = 20.4$ atmospheres can be obtained by the method of adjustment of A and Ψ described for the calculation of composition for the carbon-hydrogen-oxygen-nitrogen system.

REFERENCES

1. Zeise, H.: Thermodynamische Berschnung von Verbrennungstemperaturen und Unsätzen in Gasgemischen bei strenger Berücksichtigung aller Spallungsmöglichkeiten. Feuerungstechnik, Jg. 26, Heft 5, 15, Mai 1938, S. 145.
2. Hershey, R. L., Eberhardt, J. E., Hottel, H. C.: Thermodynamic Properties of the Working Fluid in Internal-Combustion Engines. SAE Trans., vol. 39, no. 4, Oct. 1936, pp. 409-424.
3. Hirschfelder, J. O., McClure, F. T., Curtiss, C. F., and Osborne, D. W.: Thermodynamic Properties of Propellant Gases. NDRC Rep. No. A-116, Nov. 23, 1942. (Extension and Revision of NDRC Rep. No. A-48 (OSRD No. 547).)(Abs. Bib. Sci. & Ind. Repts., vol. 2, no. 10, Sept. 6, 1946, p. 743, PB 28531.)

TABLE I - EQUILIBRIUM CONSTANTS

[Data obtained from reference 3. $\Psi = P_{H_2O}/P_{H_2}$]

Temperature (°K)	$K_1 \frac{P_{CO} \Psi}{P_{CO_2}}$	$K_3 \frac{P_{NO}}{\Psi \sqrt{P_{N_2}}}$	$K_6 \frac{P_{O_2}}{\Psi^2}$	$K_7 \frac{P_O}{\Psi}$	$K_8 \frac{P_N}{\sqrt{P_{N_2}}}$	$K_9 \frac{P_H}{\sqrt{P_{H_2}}}$	$K_{10} \frac{P_{OH}}{\Psi \sqrt{P_{H_2}}}$
2000	4.782	5.736×10^{-6}	8.139×10^{-8}	2.086×10^{-7}	8.874×10^{-7}	1.623×10^{-3}	1.636×10^{-4}
2100	5.149	1.531×10^{-5}	3.425×10^{-7}	8.847×10^{-7}	2.528×10^{-6}	3.109×10^{-3}	3.682×10^{-4}
2200	5.420	3.785×10^{-5}	1.307×10^{-6}	3.345×10^{-6}	6.544×10^{-6}	8.620×10^{-3}	8.031×10^{-4}
2300	5.853	8.373×10^{-5}	4.173×10^{-6}	1.093×10^{-5}	1.562×10^{-5}	9.662×10^{-3}	1.561×10^{-3}
2400	6.140	1.771×10^{-4}	1.260×10^{-5}	3.307×10^{-5}	3.469×10^{-5}	1.588×10^{-2}	2.939×10^{-3}
2500	6.440	3.512×10^{-4}	3.452×10^{-5}	9.121×10^{-5}	7.231×10^{-5}	2.514×10^{-2}	5.230×10^{-3}
2600	6.668	6.644×10^{-4}	8.848×10^{-5}	2.337×10^{-4}	1.428×10^{-4}	3.835×10^{-2}	8.954×10^{-3}
2700	6.954	1.188×10^{-3}	2.080×10^{-4}	5.546×10^{-4}	2.672×10^{-4}	5.674×10^{-2}	1.461×10^{-2}
2800	7.185	2.047×10^{-3}	4.638×10^{-4}	1.243×10^{-3}	4.795×10^{-4}	8.173×10^{-2}	2.308×10^{-2}
2900	7.376	3.414×10^{-3}	9.883×10^{-4}	2.646×10^{-3}	8.267×10^{-4}	.1148	3.550×10^{-2}
3000	7.582	5.479×10^{-3}	1.983×10^{-3}	5.336×10^{-3}	1.373×10^{-3}	.1579	5.290×10^{-2}
3100	7.748	8.525×10^{-3}	3.803×10^{-3}	1.027×10^{-2}	2.210×10^{-3}	.2125	7.677×10^{-2}
3200	7.929	1.294×10^{-2}	7.055×10^{-3}	1.904×10^{-2}	3.452×10^{-3}	.2813	.1087
3300	8.078	1.859×10^{-2}	1.248×10^{-2}	3.389×10^{-2}	5.253×10^{-3}	.3654	.1513
3400	8.192	2.758×10^{-2}	2.157×10^{-2}	5.857×10^{-2}	7.798×10^{-3}	.4682	.2060
3500	8.304	3.894×10^{-2}	3.583×10^{-2}	9.778×10^{-2}	1.132×10^{-2}	.5910	.2763
3600	8.449	5.404×10^{-2}	5.821×10^{-2}	.1591	1.611×10^{-2}	.7367	.3614
3700	8.535	7.355×10^{-2}	9.166×10^{-2}	.2516	2.248×10^{-2}	.9084	.4691
3800	8.664	9.821×10^{-2}	.1412	.3876	3.086×10^{-2}	1.107	.5984
3900	8.712	.1300	.2134	.5878	4.166×10^{-2}	1.336	.7589
4000	8.752	.1693	.3157	.8711	5.544×10^{-2}	1.597	.9495
4100	8.819	.2162	.4526	1.258	7.258×10^{-2}	1.893	1.164
4200	8.884	.2760	.6519	1.808	9.423×10^{-2}	2.226	1.428
4300	8.898	.3463	.9139	2.537	.1206	2.598	1.730
4400	8.929	.4302	1.263	3.508	.1528	3.012	2.089
4500	8.952	.5291	1.718	4.778	.1916	3.470	2.478
4600	8.974	.6451	2.307	6.431	.2379	3.969	2.923
4700	8.984	.7799	3.068	8.545	.2927	4.520	3.432
4800	8.994	.9344	4.015	11.21	.3570	5.118	3.992
4900	9.003	1.115	5.228	14.59	.4321	5.764	4.637
5000	9.012	1.317	6.693	18.77	.5193	6.461	5.317

NACA

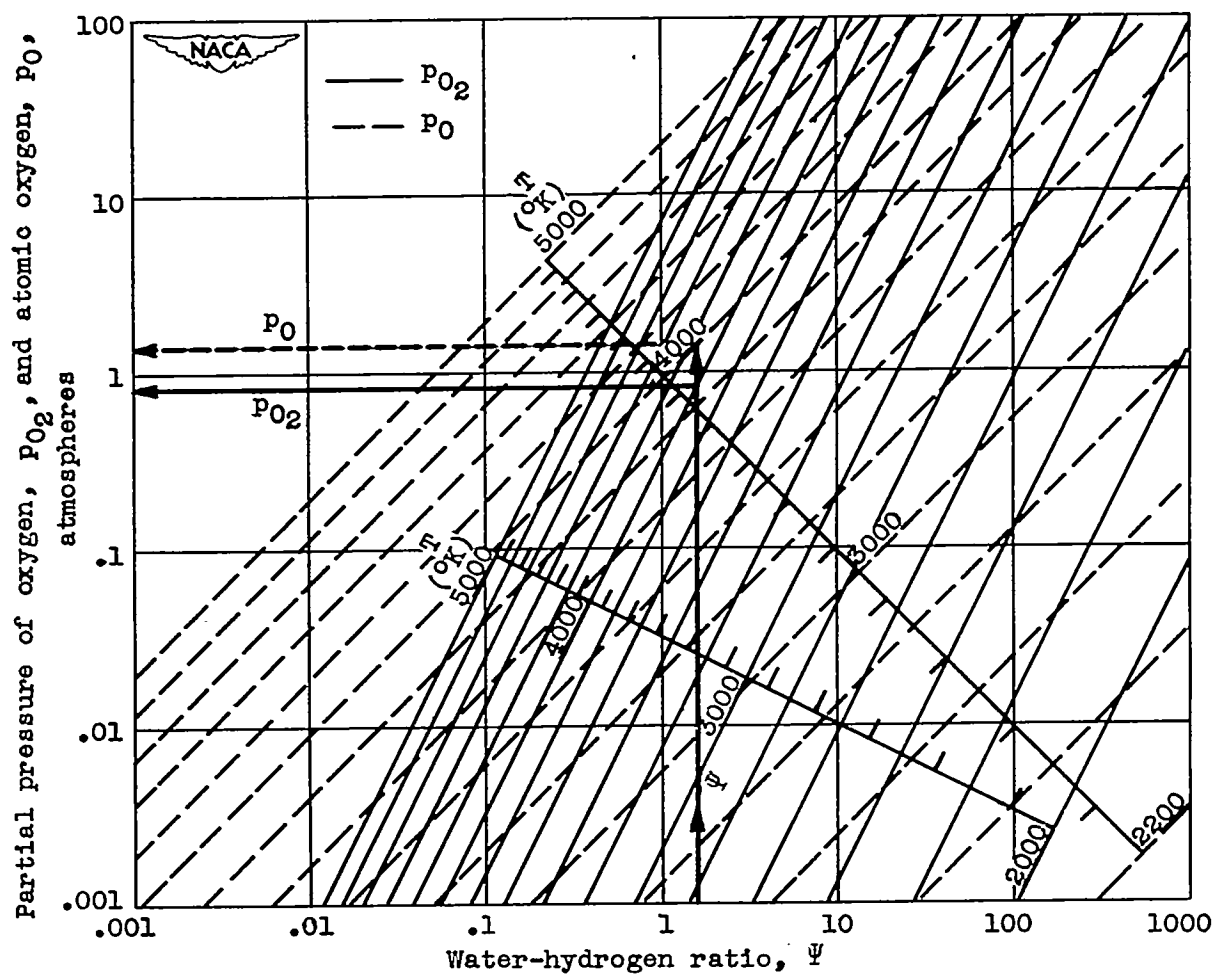
TABLE II - RESULTS OF SAMPLE CALCULATION OF THE REACTION
 $C_2H_4(NH_2)_2 + 4O_2 \rightarrow \text{PRODUCTS}$

$[w = 2, x = 8, y = 8, z = 2, \Sigma = 7, r = 1.00, T = 4000^\circ K, P = 10,$
 $K_1 = 8.752, K_3 = 0.1693, K_6 = 0.3157, K_7 = 0.8711, K_8 = 0.0554,$
 $K_9 = 1.507, K_{10} = 0.9495]$

Quantity	Arithmetical			Graphical		
	Source	First trial	Second trial	Source	First trial	Second trial
Ψ	Figure 2(c)	1.6	1.4	Figure 2(c)	1.6	1.4
$A\Sigma/P_1$	Figure 2(c)	.84	.81	Figure 2(c)	.84	.81
P_{O_2}	Equation (36)	.8082	.6188	Figure 1(a)	.81	.62
P_O	Equation (37)	1.3938	1.2195	Figure 1(a)	1.39	1.22
P_1	Equation (5)	7.7980	8.1617	Equation (5)	7.80	8.16
A	Equation (7)	.9358	.9444	Equation (7)	.936	.944
$Ax/(\Psi+1)$	(a)	2.8793	3.1480	(a)	2.88	3.146
a	Equation (39)	1.1985	1.2193			
P_{H_2}	Equation (40)	.8782	.9728	Figure 1(b)	.88	.97
P_{OH}	Equation (45)	1.4236	1.3111	Figure 1(c)	1.42	1.31
P_H	Equation (46)	1.4965	1.5751	Figure 1(c)	1.50	1.57
P_{H_2O}	Equation (44)	1.4051	1.3619	Equation (44)	1.408	1.358
Az	(a)	1.8716	1.8888	(a)	1.872	1.888
b	Equation (42)	.3263	.2925			
P_{N_2}	Equation (43)	.7907	.8127	Figure 1(d)	.79	.81
P_{NO}	Equation (47)	.2409	.2137	Figure 1(e)	.241	.214
P_N	Equation (48)	.0493	.0500	Figure 1(e)	.049	.05
Aw	(a)	1.8716	1.8888	(a)	1.872	1.888
P_{CO_2}	Equation (49)	.2893	.2605	Figure 1(f)	.290	.260
P_{CO}	Equation (50)	1.5823	1.6254	Equation (50)	1.582	1.628
P'	Equation (2)	10.3579	10.0244	Equation (2)	10.360	10.01
Ay'	Equation (3)	8.2407	7.4931	Equation (3)	8.241	7.49
r'	Equation (8)	.9085	1.0083	Equation (8)	.9086	1.008
P'_1	Equation (9)	8.1559	-----	Equation (9)	8.160	-----
$A\Sigma/P'_1$	$A\Sigma/P'_1$.8032	-----	$A\Sigma/P'_1$.803	-----

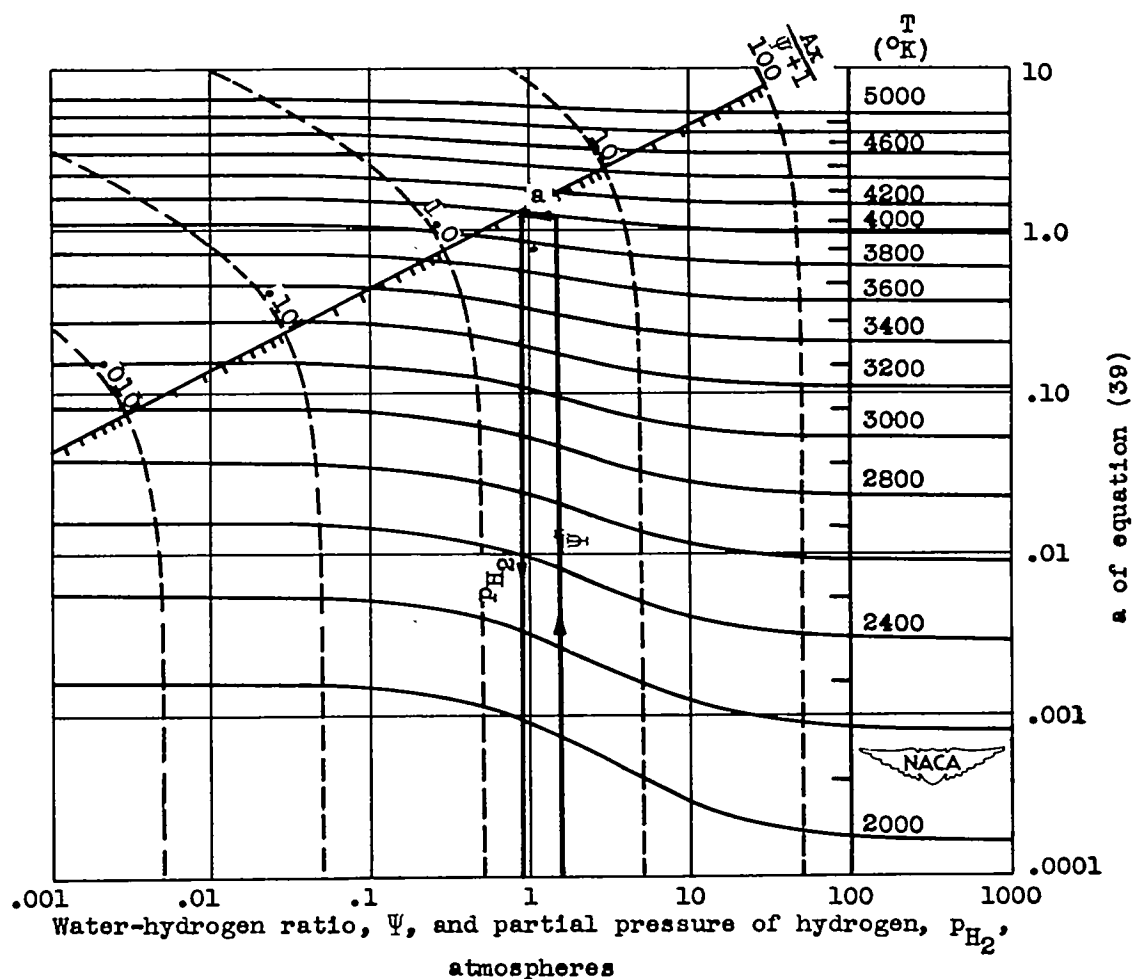
^aNumerical calculation.

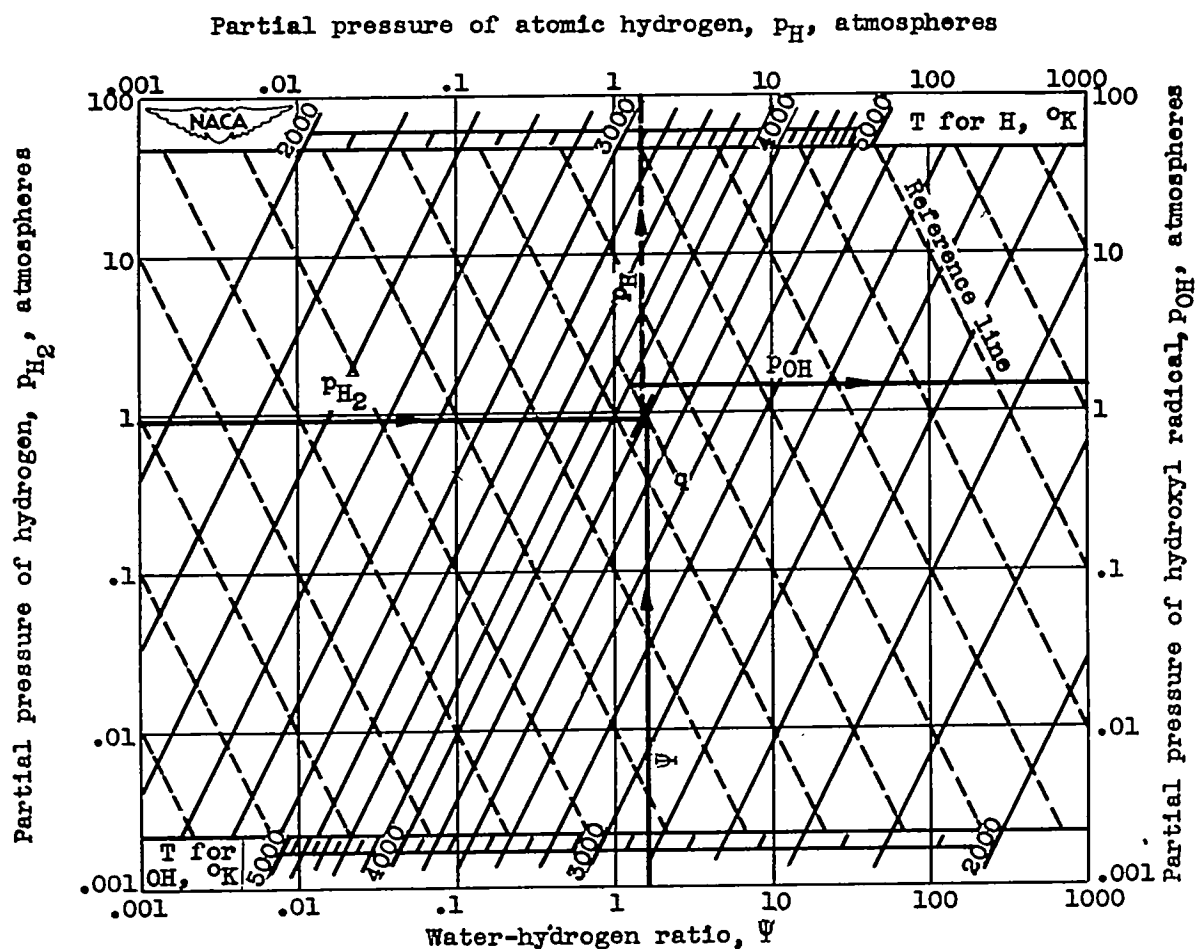




(a) Partial pressures of oxygen p_{O_2} and atomic oxygen p_O .

Figure 1. - Partial-pressure computation charts. $\Psi = p_{H_2O}/p_{H_2}$. (A 17- by 20-inch print of this figure is attached.)

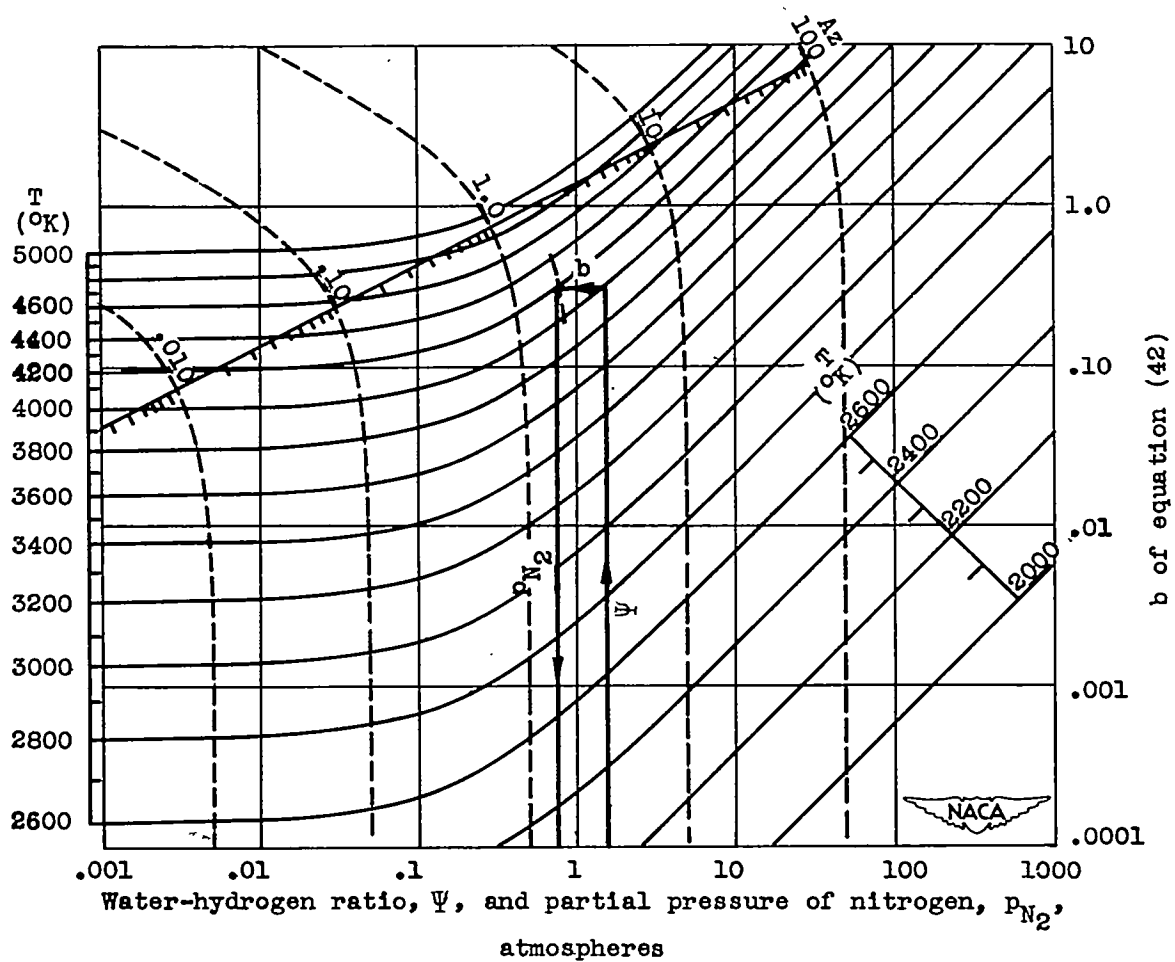




(c) Partial pressures of hydroxyl radical P_{OH} and atomic hydrogen P_H .

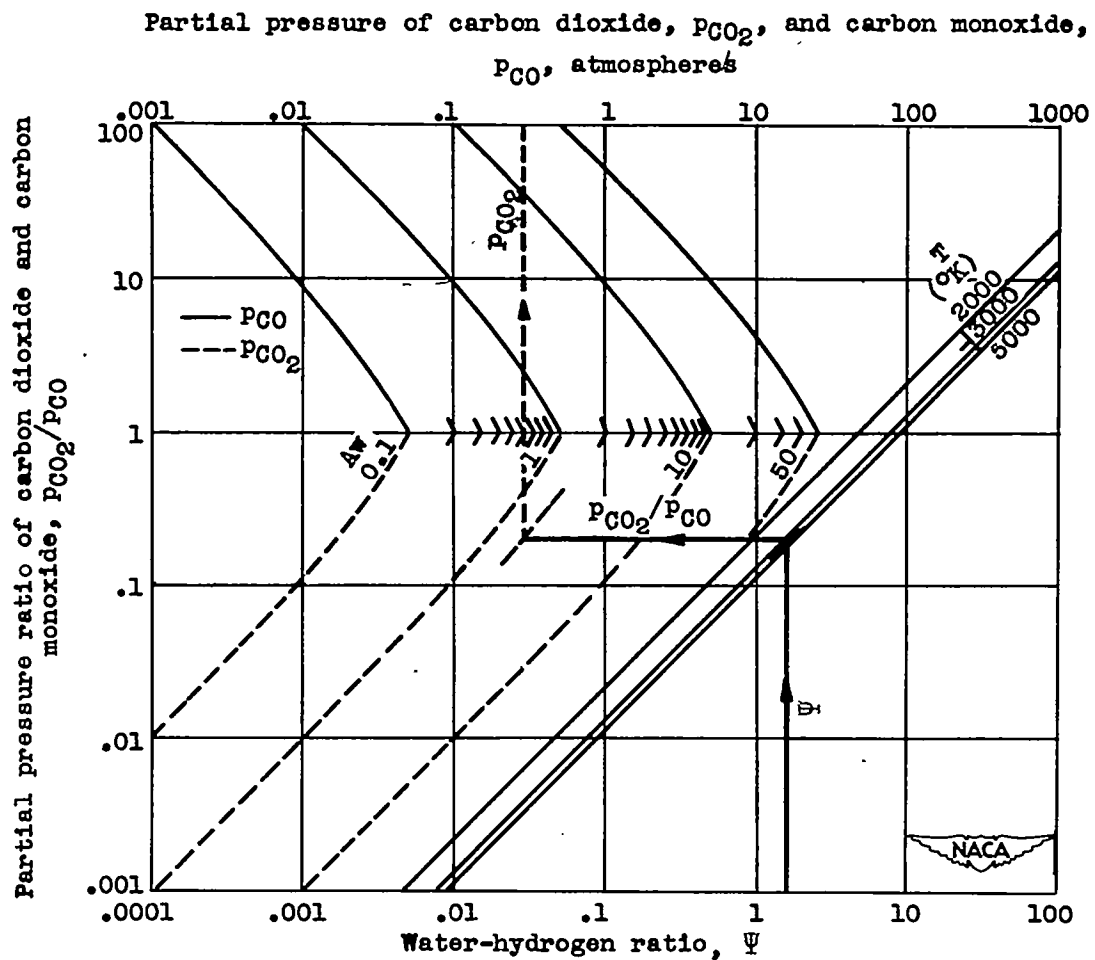
Figure 1. - Continued. Partial-pressure computation charts.
 $\Psi = P_{H_2O}/P_{H_2}$

(A 17- by 20-inch print of this figure is attached.)



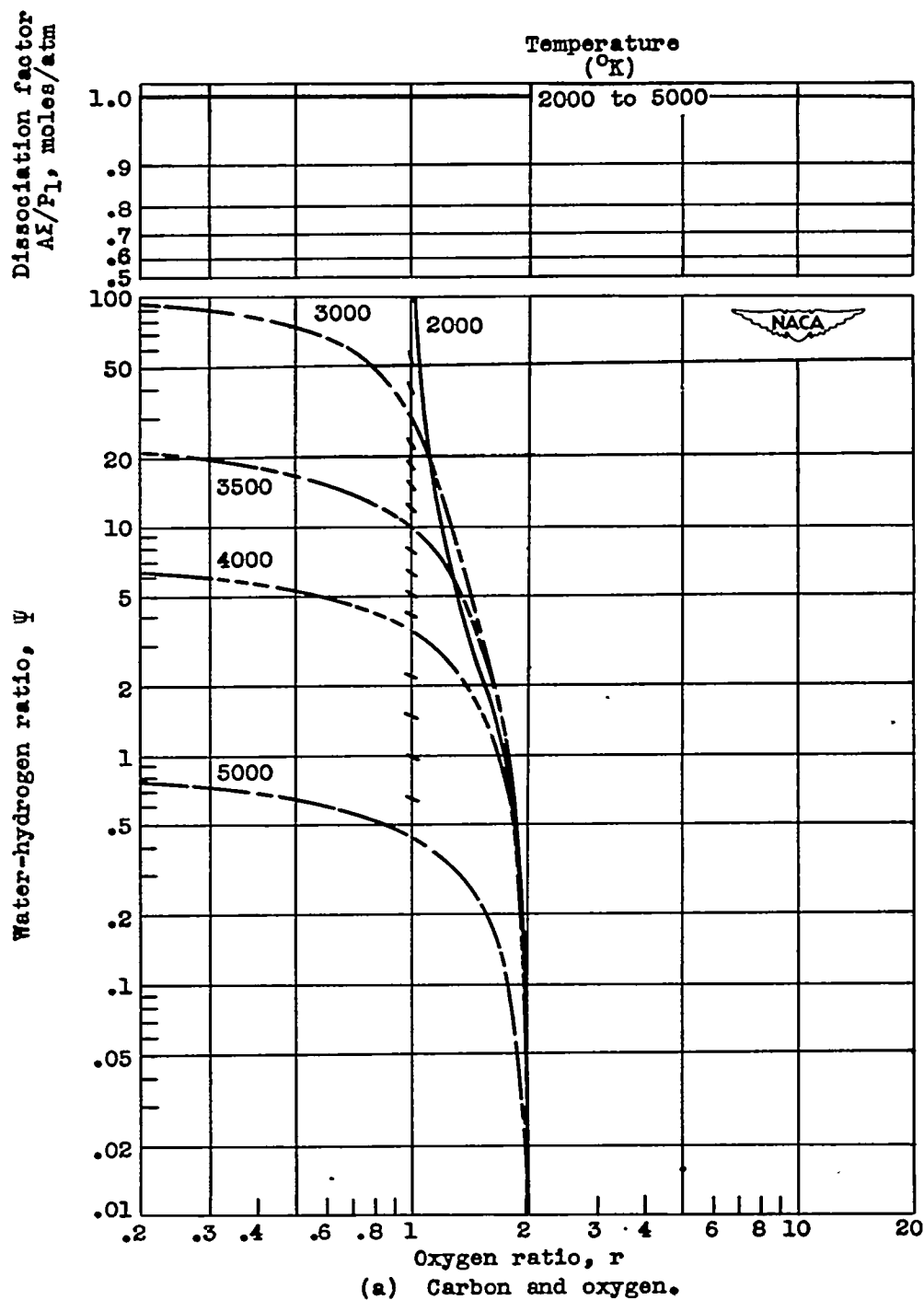
(d) Partial pressure of nitrogen p_{N_2} . Number of atoms of nitrogen Az.

Figure 1. - Continued. Partial-pressure computation charts. $\Psi = p_{H_2O}/p_{H_2}$.
(A 17- by 20-inch print of this figure is attached.)



(f) Partial pressures of carbon dioxide p_{CO_2} and carbon monoxide p_{CO} . Number of atoms of carbon A_w .

Figure 1. - Concluded. Partial-pressure computation charts. $\Psi = p_{H_2O}/p_{H_2}$.
(A 17- by 20-inch print of this figure is attached.)



(a) Carbon and oxygen.

Figure 2. - Variation of water-hydrogen ratio Ψ and dissociation factor AE/P_1 with oxygen ratio r at a pressure of 20.4 atmospheres. $\Psi = P_{H_2O}/P_{H_2}$. (An 11- by 17-inch print of this figure is attached.)

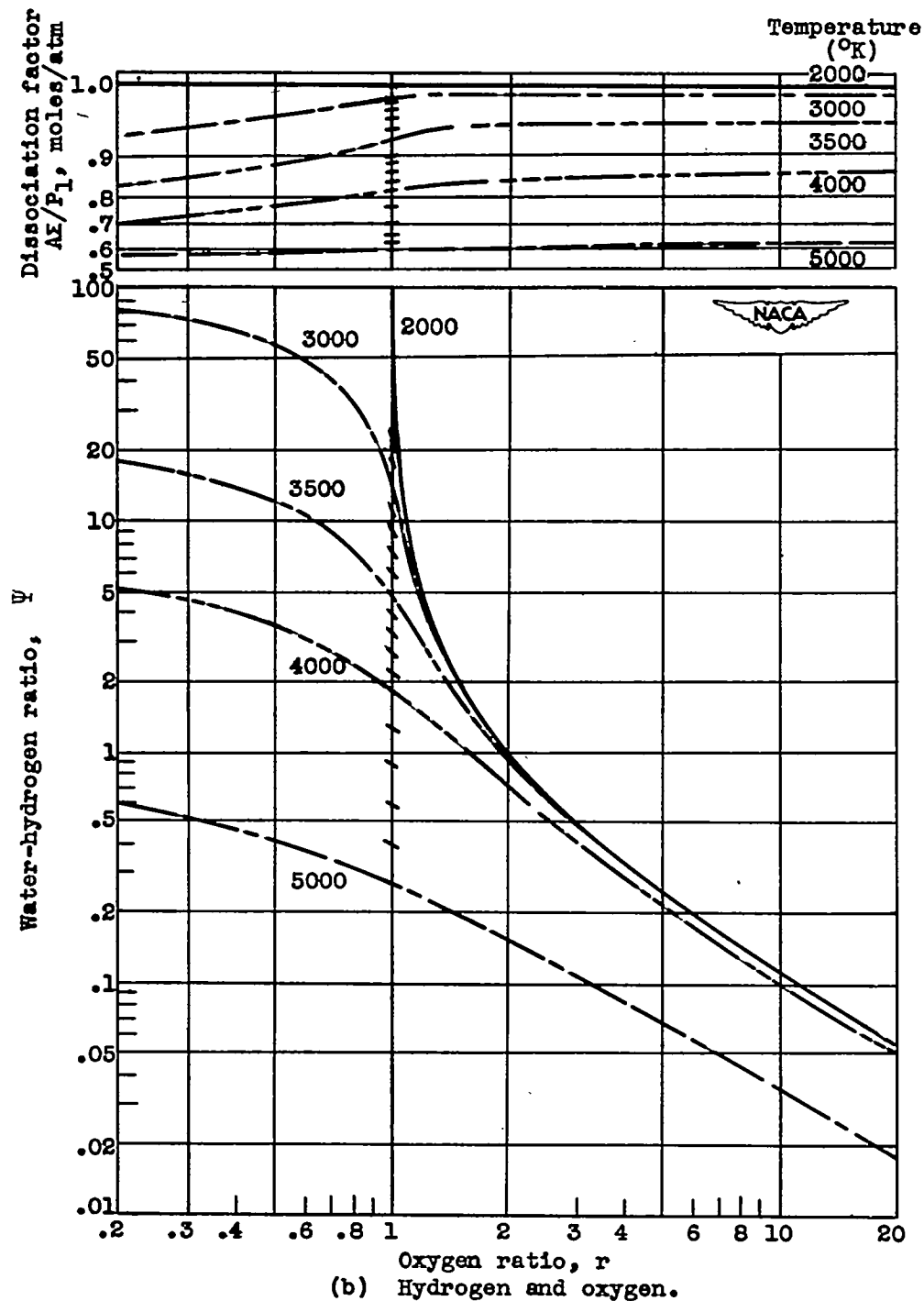
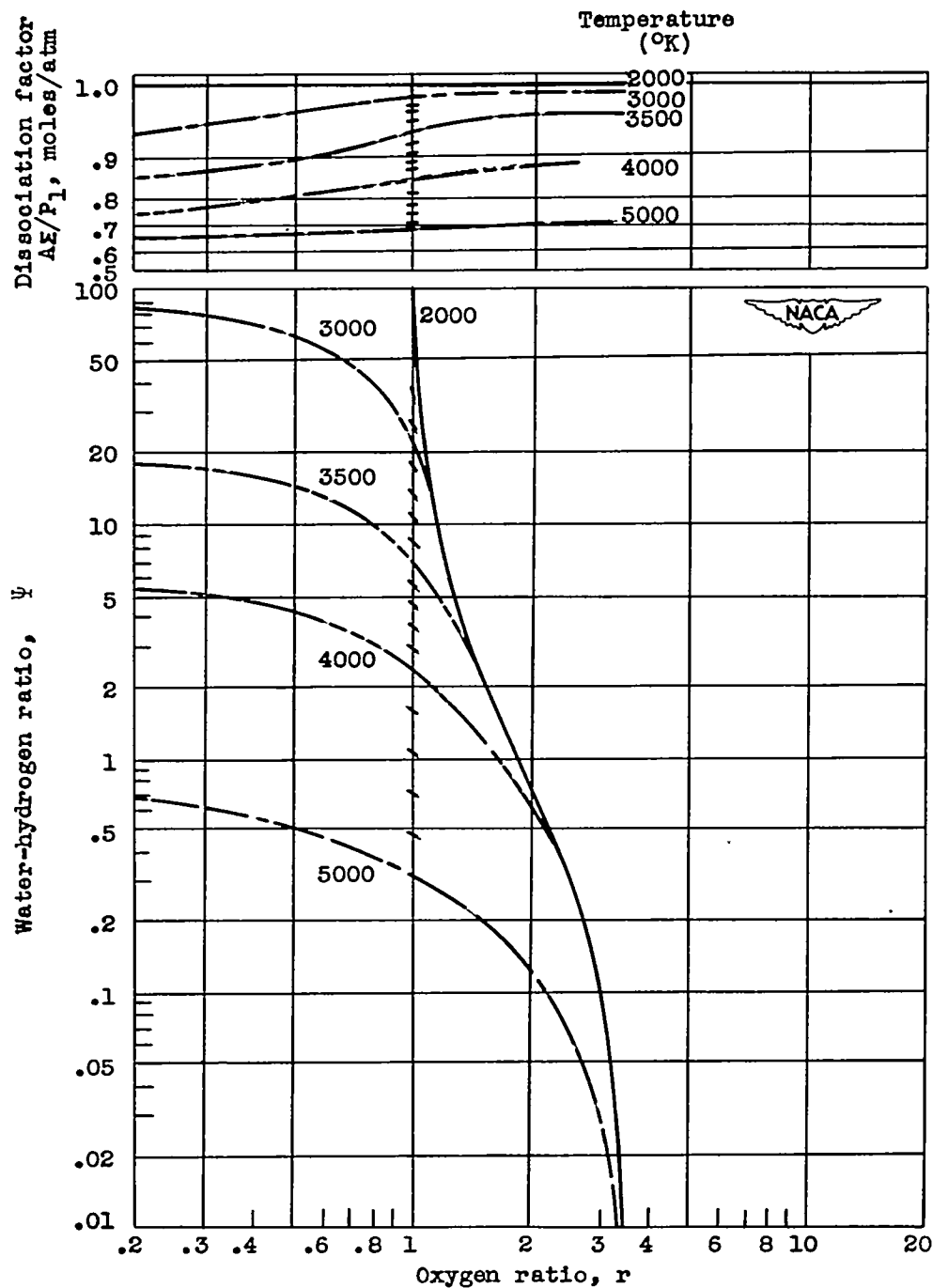
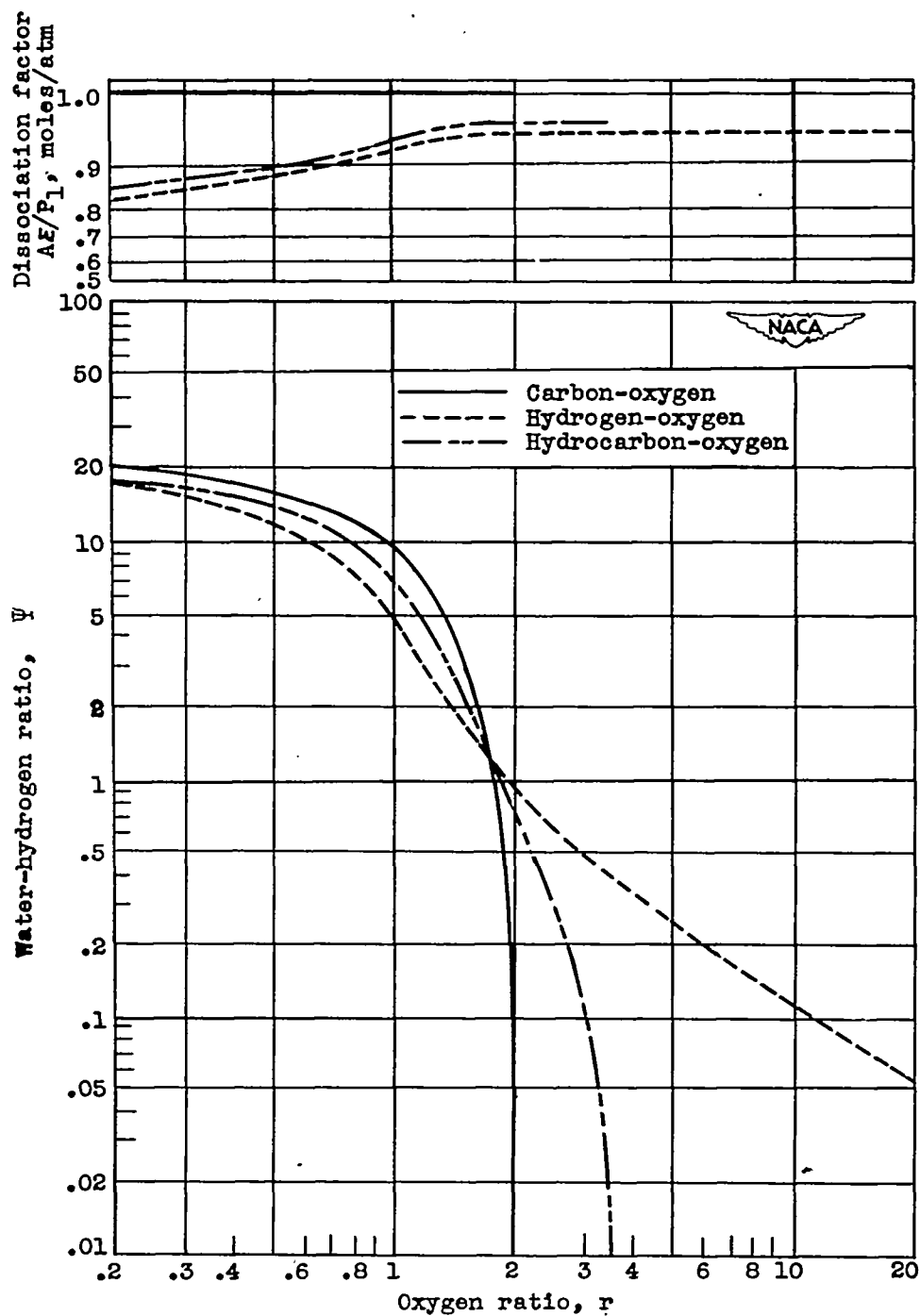


Figure 2. - Continued. Variation of water-hydrogen ratio Ψ and dissociation factor $\frac{AE}{P_1}$ with oxygen ratio r at a pressure of 20.4 atmospheres. $\Psi = \frac{P_{H_2O}}{P_{H_2}}$. (An 11- by 17-inch print of this figure is attached.)



(c) Hydrocarbon and oxygen with a hydrogen-to-carbon atom ratio of 3.

Figure 2. - Continued. Variation of water-hydrogen ratio Ψ and dissociation factor AE/P_1 with oxygen ratio r at a pressure of 20.4 atmospheres. $\Psi = P_{H_2O}/P_{H_2}$. (An 11- by 17-inch print of this figure is attached.)



(d) Carbon-, hydrogen-, and hydrocarbon-oxygen at temperature of 3500° K.

Figure 2. - Concluded. Variation of water-hydrogen ratio Ψ and dissociation factor AE/P_1 with oxygen ratio r at a pressure of 20.4 atmospheres. $\Psi = P_{H_2O}/P_{H_2}$.

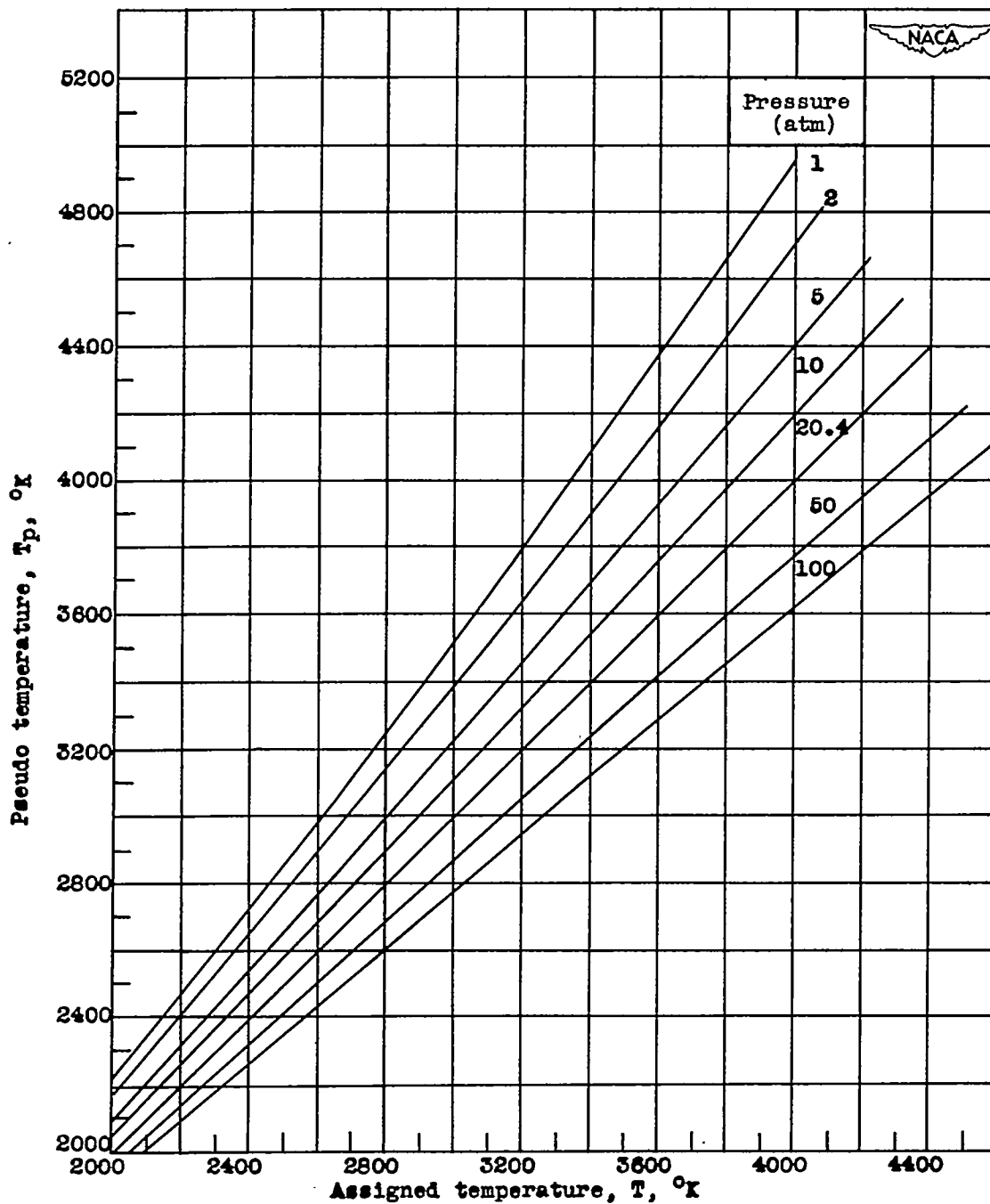


Figure 3. - Chart permitting figure 2 to be used over range of pressures.
(Pseudo-temperature value is used in fig. 2.)

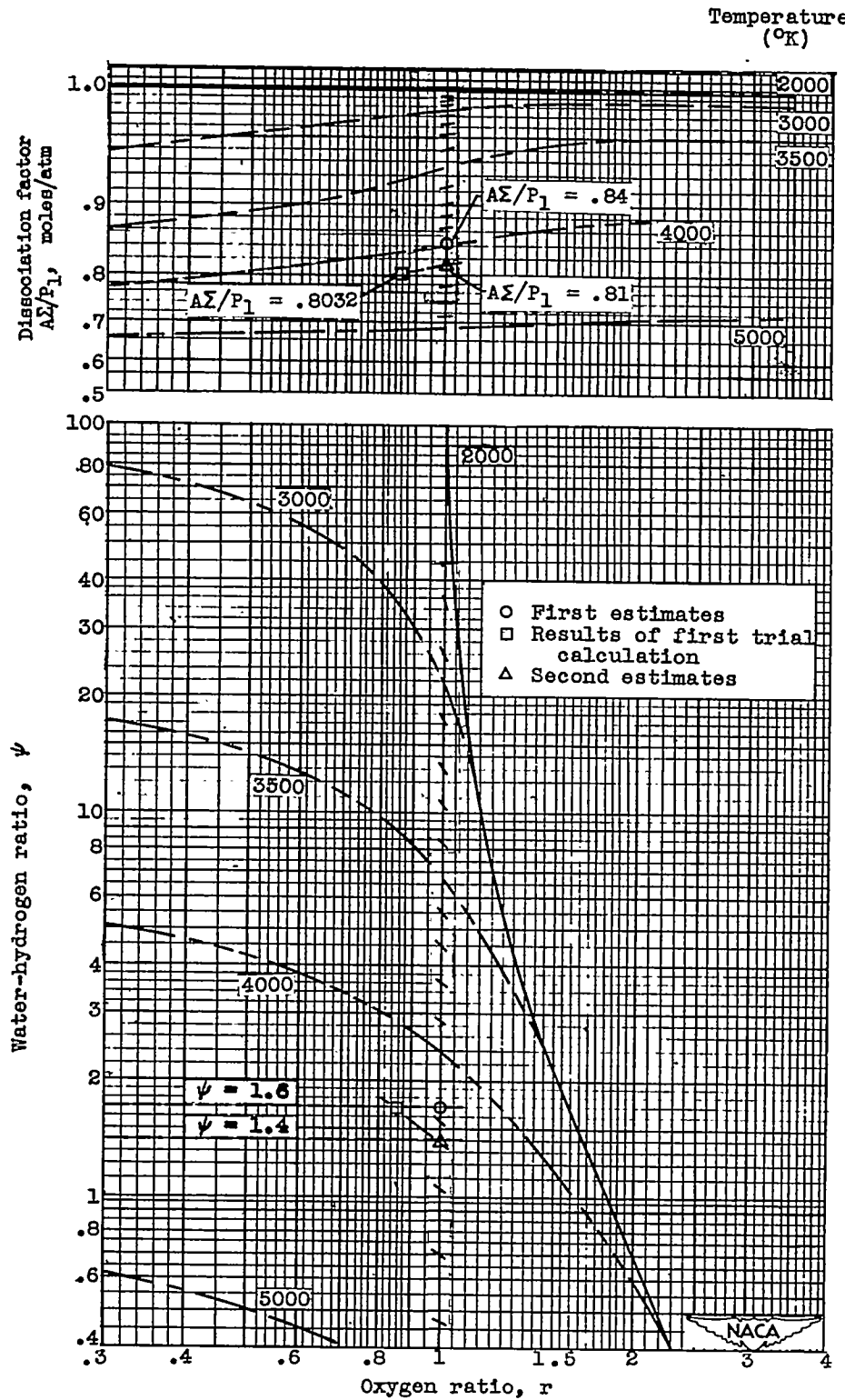
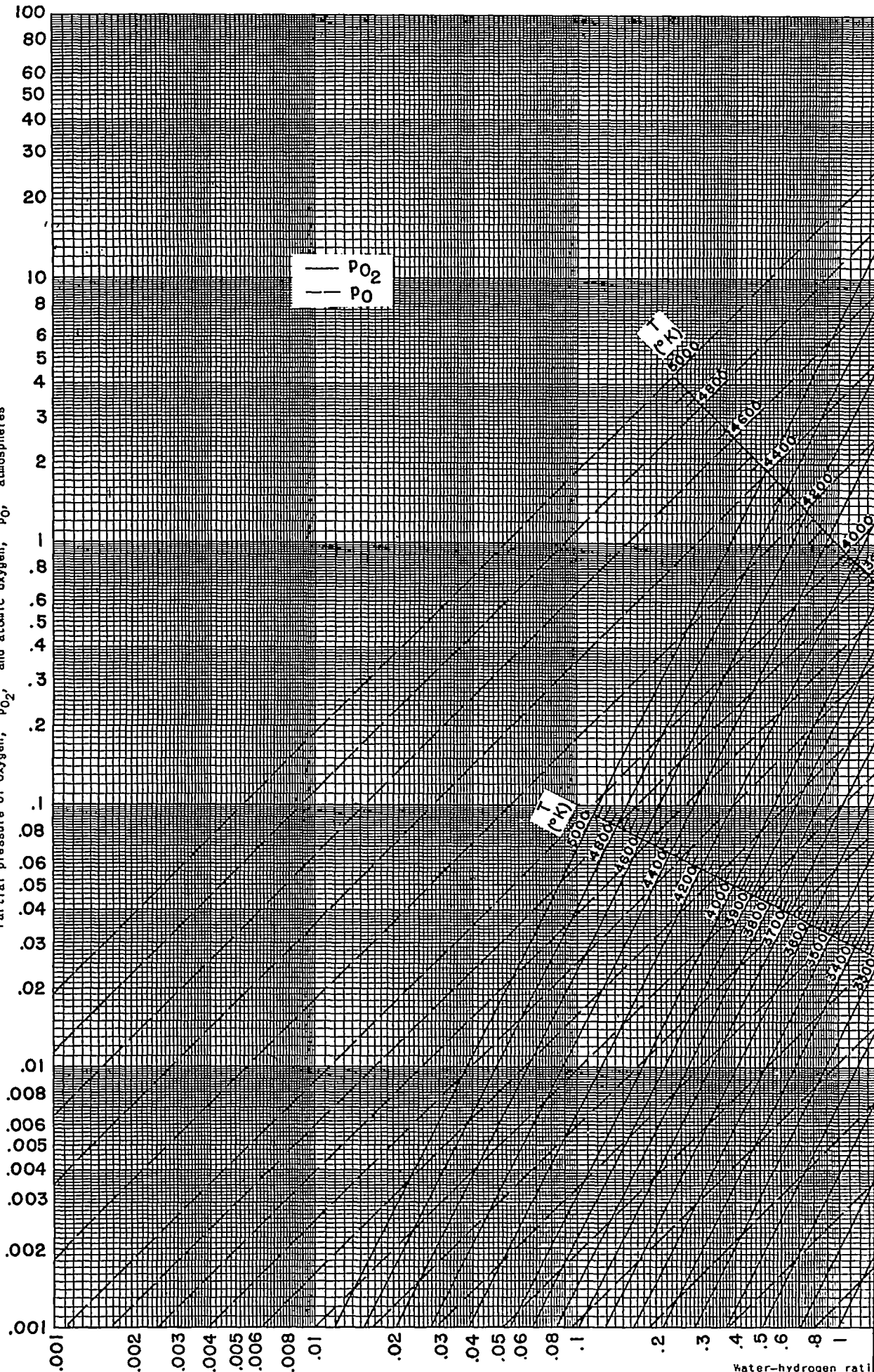


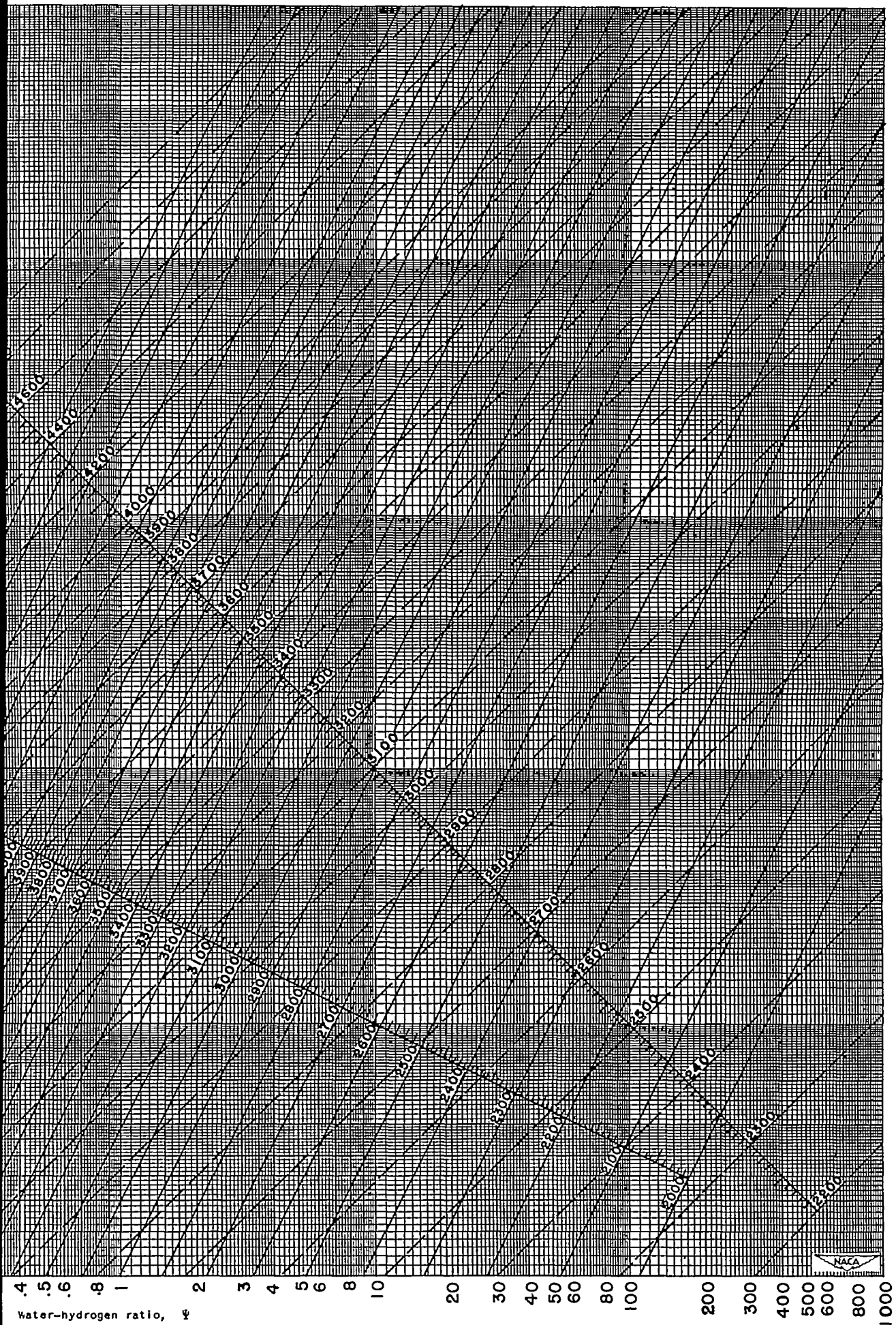
Figure 4. - Application of figure 2(c) to example, ethylenediamine $\text{C}_2\text{H}_4(\text{NH}_2)_2$ reacting with oxygen O_2 . $\psi = P_{\text{H}_2\text{O}}/P_{\text{H}_2}$. Pressure, 10 atmospheres; temperature, 4000°K .

Partial pressure of oxygen, P_{O_2} , and atomic oxygen, P_O , atmospheres



(a) Partial pressures of oxygen P_{O_2}

Figure 1. - Partial-pressure computation



Water-hydrogen ratio, Ψ
 pressures of oxygen p_{O_2} and atomic oxygen p_O .
 1-pressure computation charts. $\Psi = p_{H_2O}/p_{H_2}$.

Water-hydrogen ratio, Ψ , and partial pressure of hydrogen,

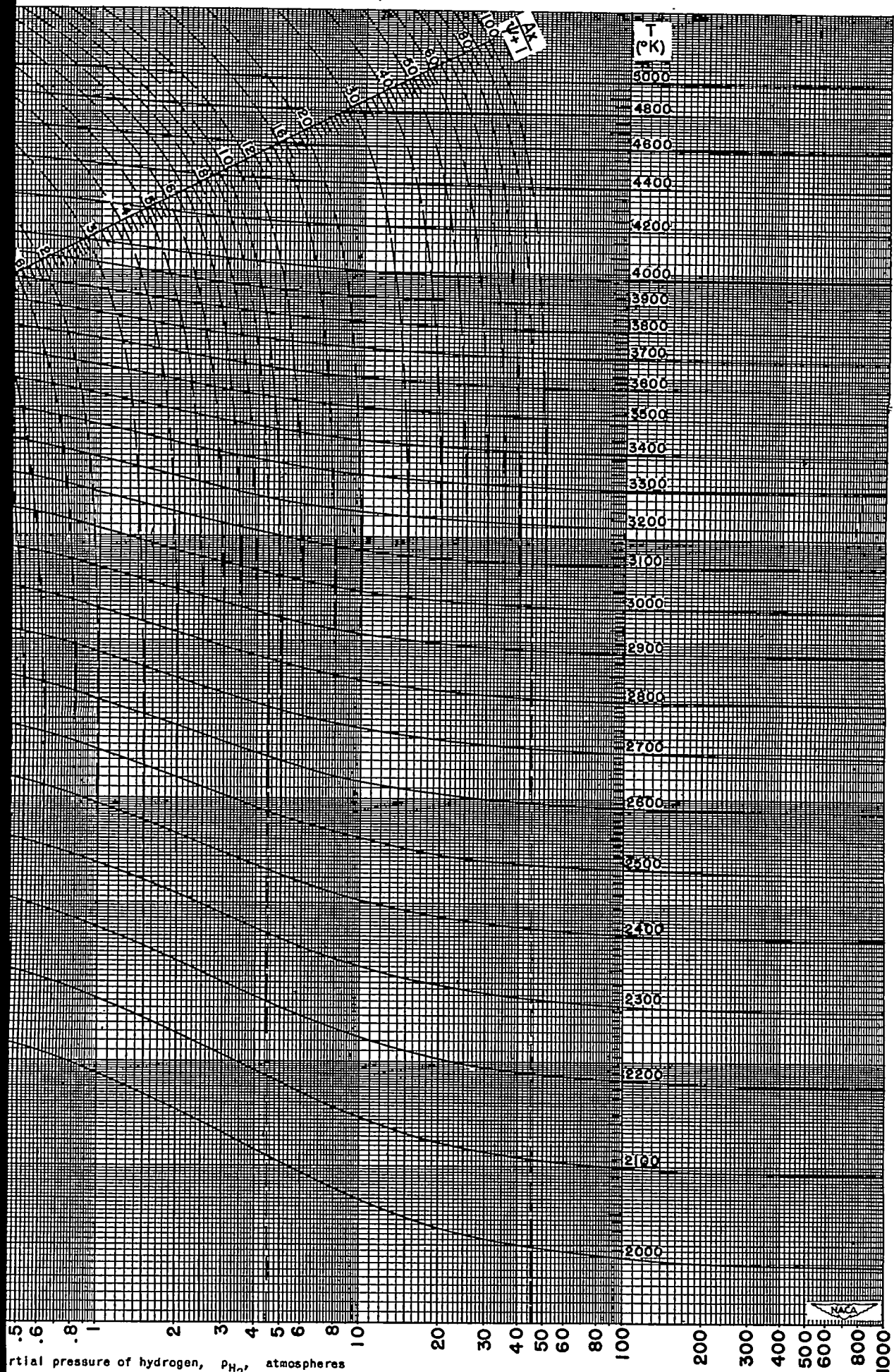
(b) Partial pressure of hydrogen p_{H_2} . Number of atoms n

Figure 1. - Continued. Partial-pressure computation charts

Water-hydrogen ratio, Ψ , and partial pressure of hydrogen,

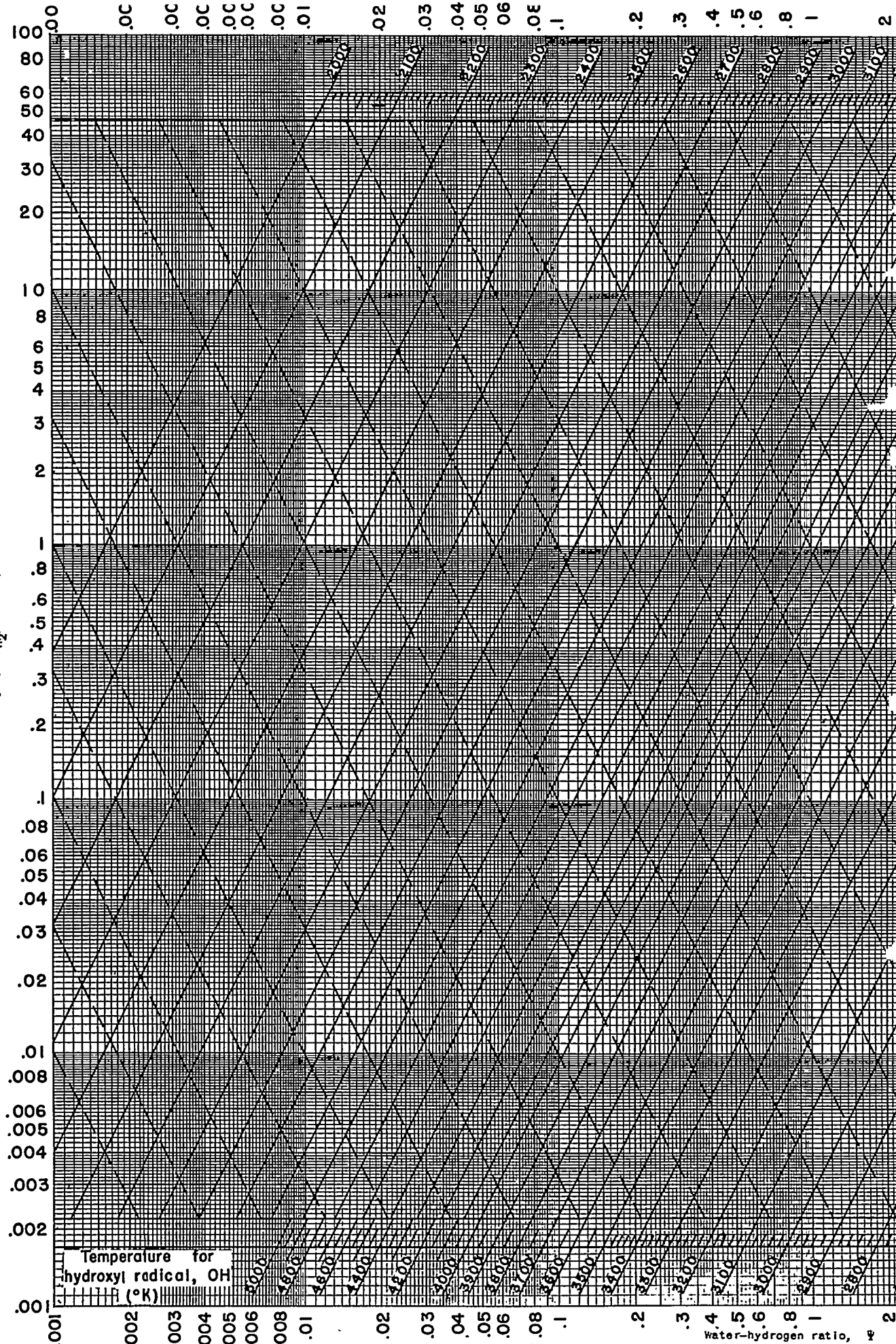
(b) Partial pressure of hydrogen p_{H_2} . Number of atoms n

Figure 1. - Continued. Partial-pressure computation charts



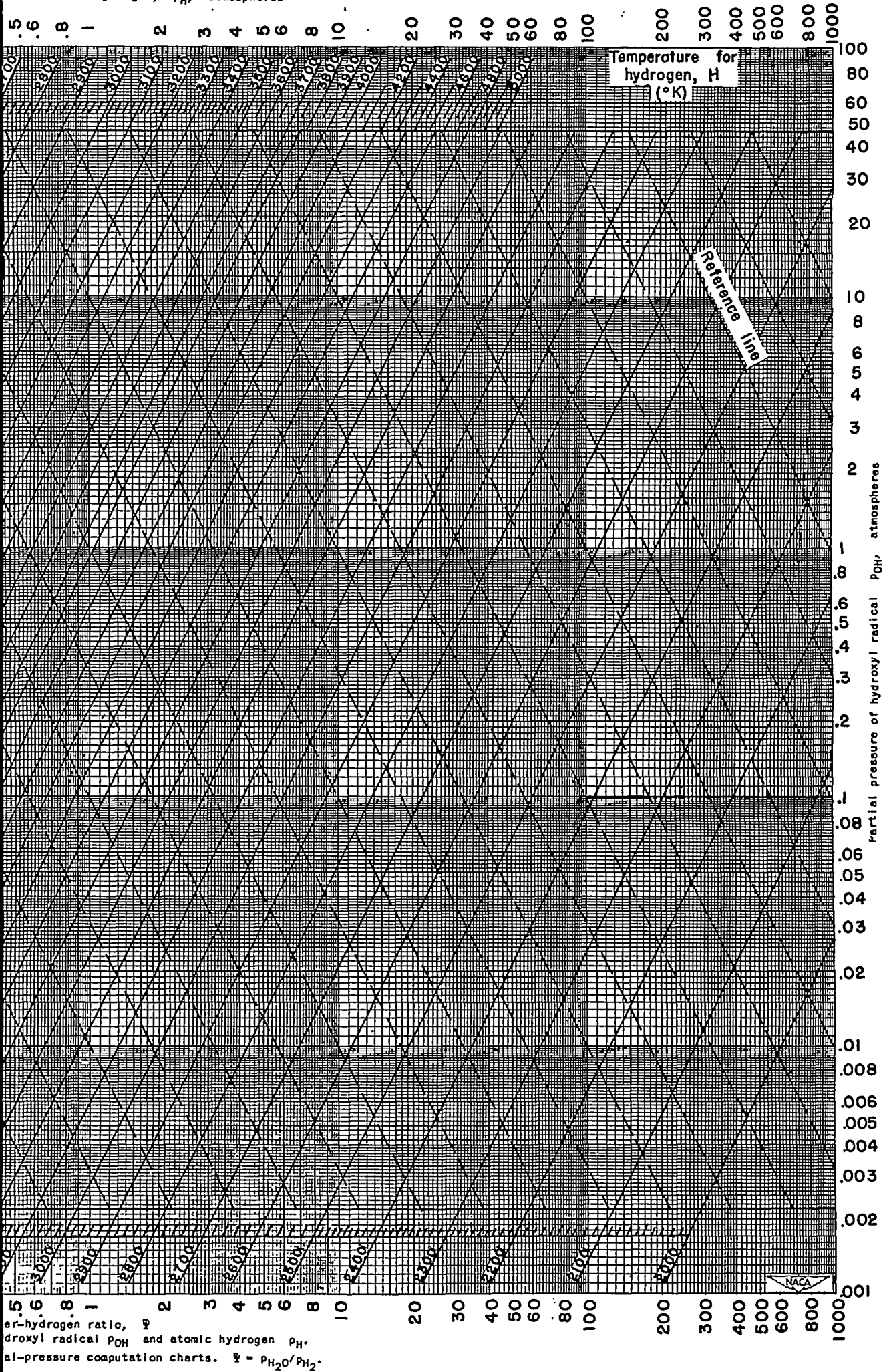
Partial pressure of hydrogen, p_{H_2} , atmospheres
 Number of atoms of hydrogen A_x .
 Pressure computation charts. $\Psi = p_{H_2O}/p_{H_2}$.

Partial pressure of hydrogen, P_{H_2} , atmospheres

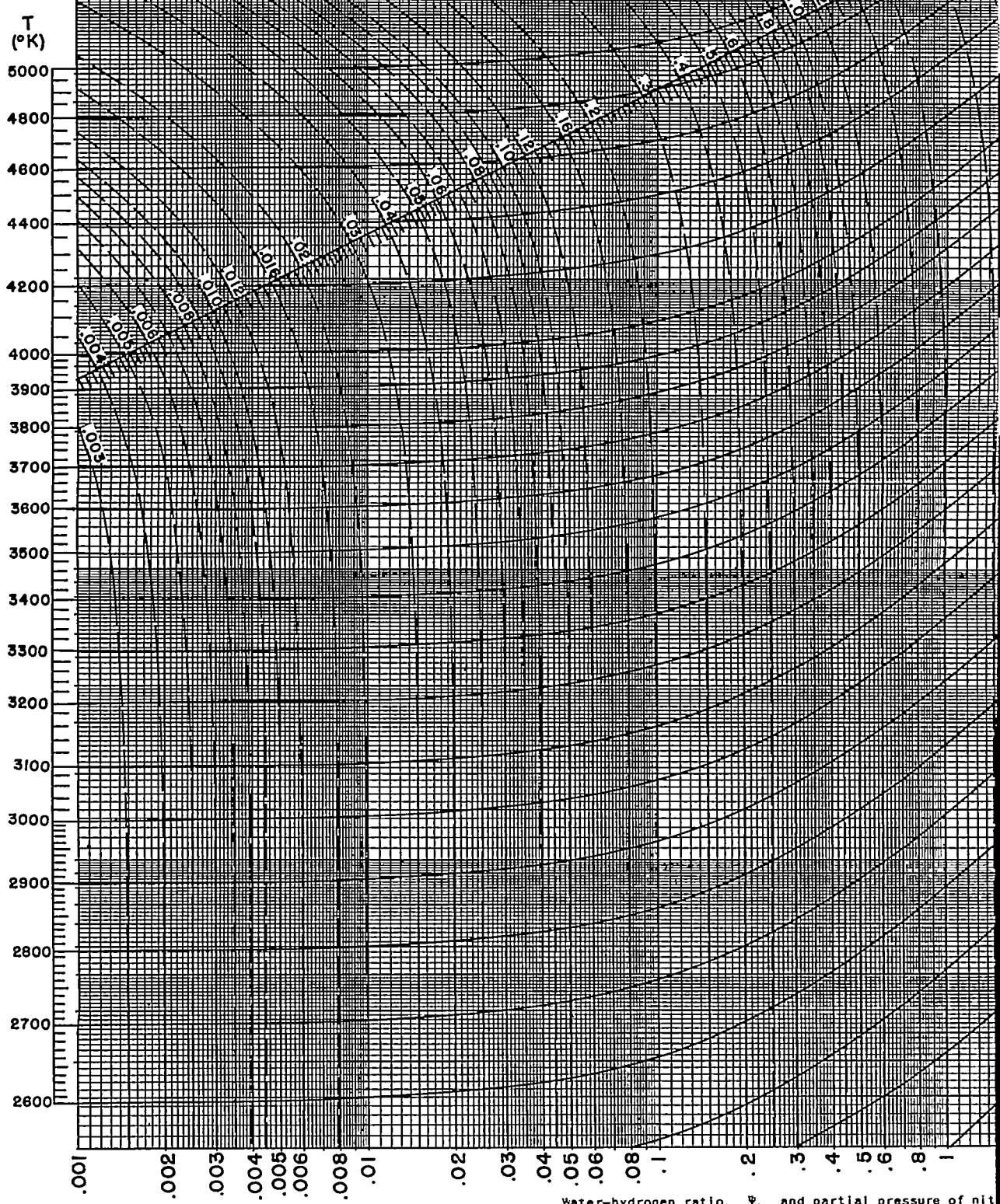


(c) Partial pressures of hydroxyl radical P_{OH} and a
Figure 1. - Continued. Partial-pressure computation c

ratio of atomic hydrogen, p_H , atmospheres

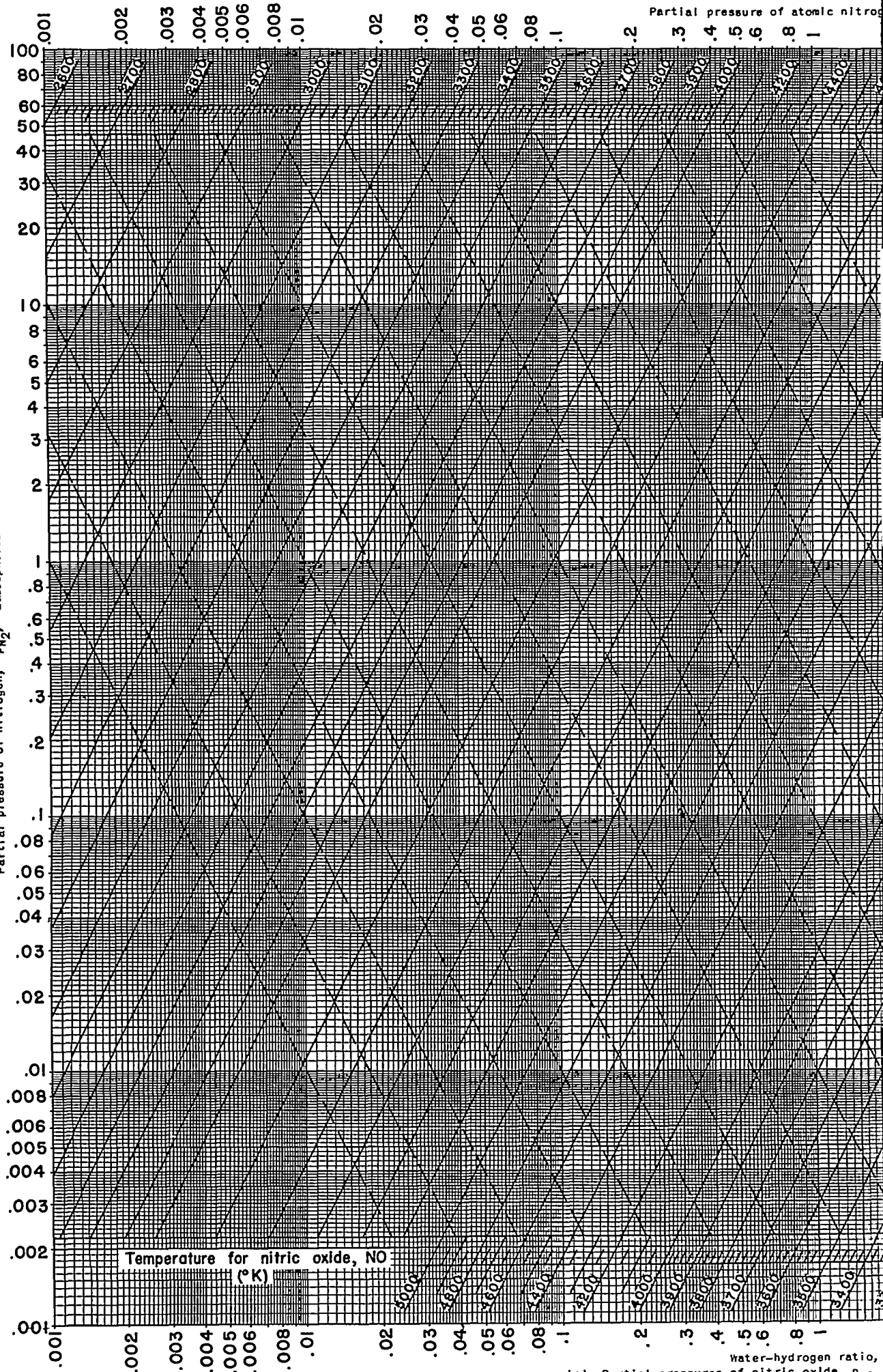


water-hydrogen ratio, $\frac{p_{H_2O}}{p_{H_2}}$
hydroxyl radical p_{OH} and atomic hydrogen p_H .
partial-pressure computation charts. $\frac{p_{H_2O}}{p_{H_2}} = \frac{p_{H_2O}}{p_{H_2}}$.



(d) Partial pressure of nitrogen p_{N_2} . Number of
Figure 1. - Continued. Partial-pressure computation

Partial pressure of nitrogen, P_{N_2} , atmospheres



(e) Partial pressures of nitric oxide P_{NO}
Figure 1. - Continued. Partial-pressure computation

Pressure of atomic nitrogen, p_N , atmospheres

0.5

0.6

0.8

1

2

3

4

5

6

8

10

20

30

40

50

60

80

100

200

300

400

500

600

800

1000

Temperature for nitrogen, N

(°K)

Partial pressure of nitric oxide, p_{NO} , atmospheres

0.001

0.002

0.003

0.004

0.005

0.006

0.008

0.01

0.02

0.03

0.04

0.05

0.06

0.08

0.1

0.2

0.3

0.4

0.5

0.6

0.8

1

2

3

4

5

6

8

10

20

30

40

50

60

80

100

200

300

400

500

600

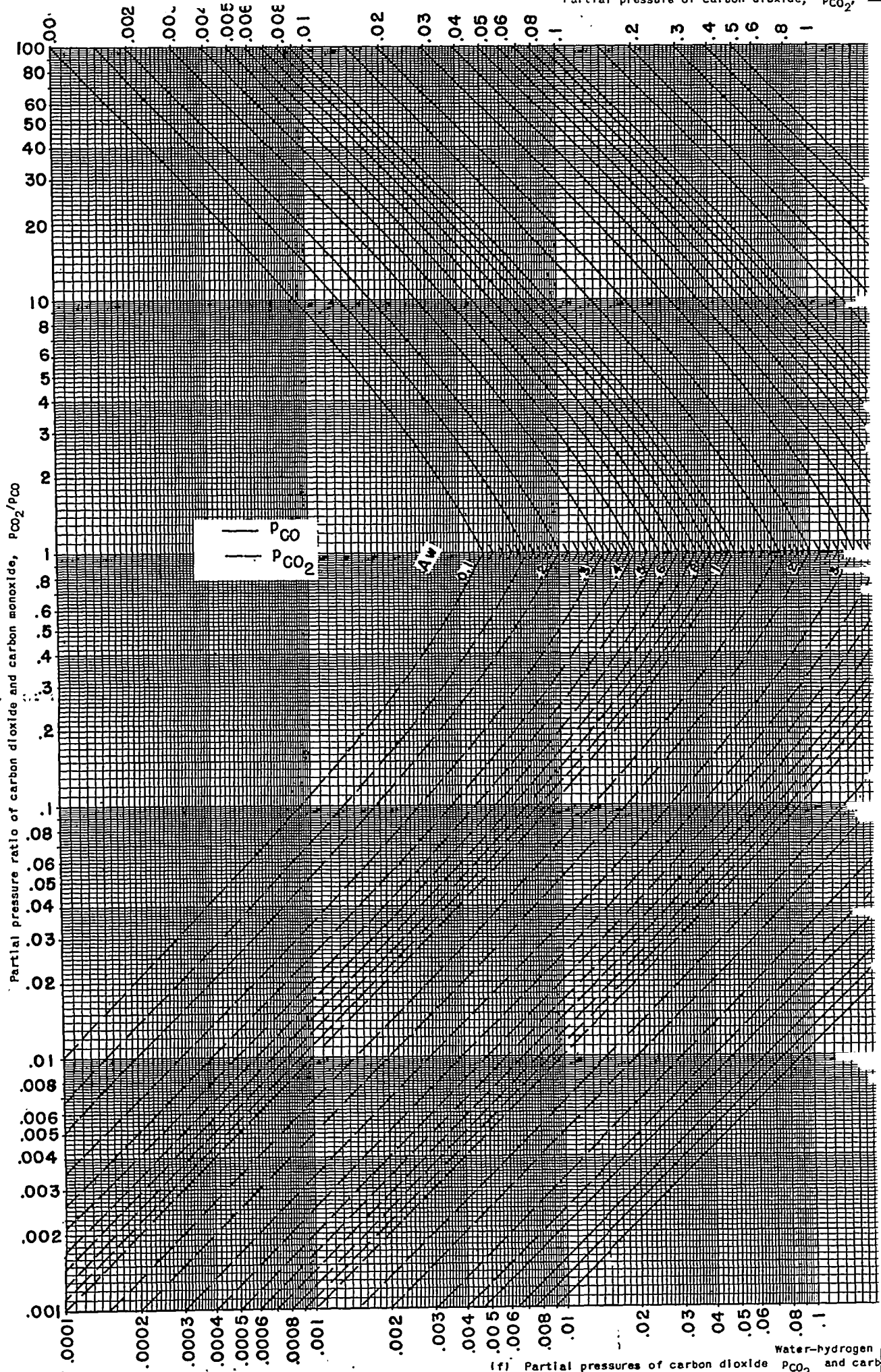
800

1000

Reference line



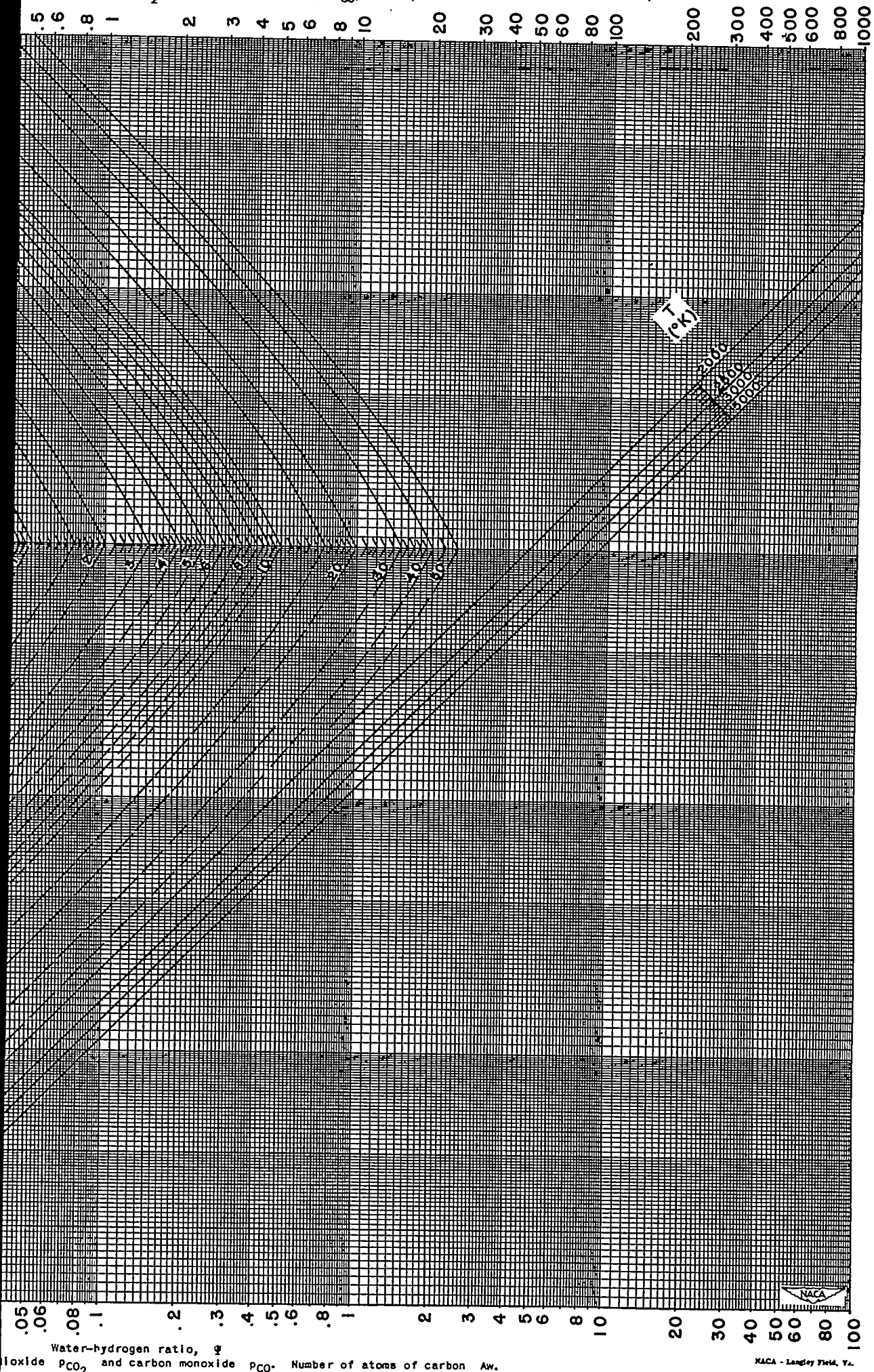
Water-hydrogen ratio, Ψ
of nitric oxide p_{NO} and atomic nitrogen p_N .



(f) Partial pressures of carbon dioxide P_{CO_2} and carbon monoxide P_{CO} and water-hydrogen ratio A_w .

Figure 1. - Concluded. Partial-pressure

Carbon dioxide, p_{CO_2} , and carbon monoxide, p_{CO} , atmospheres



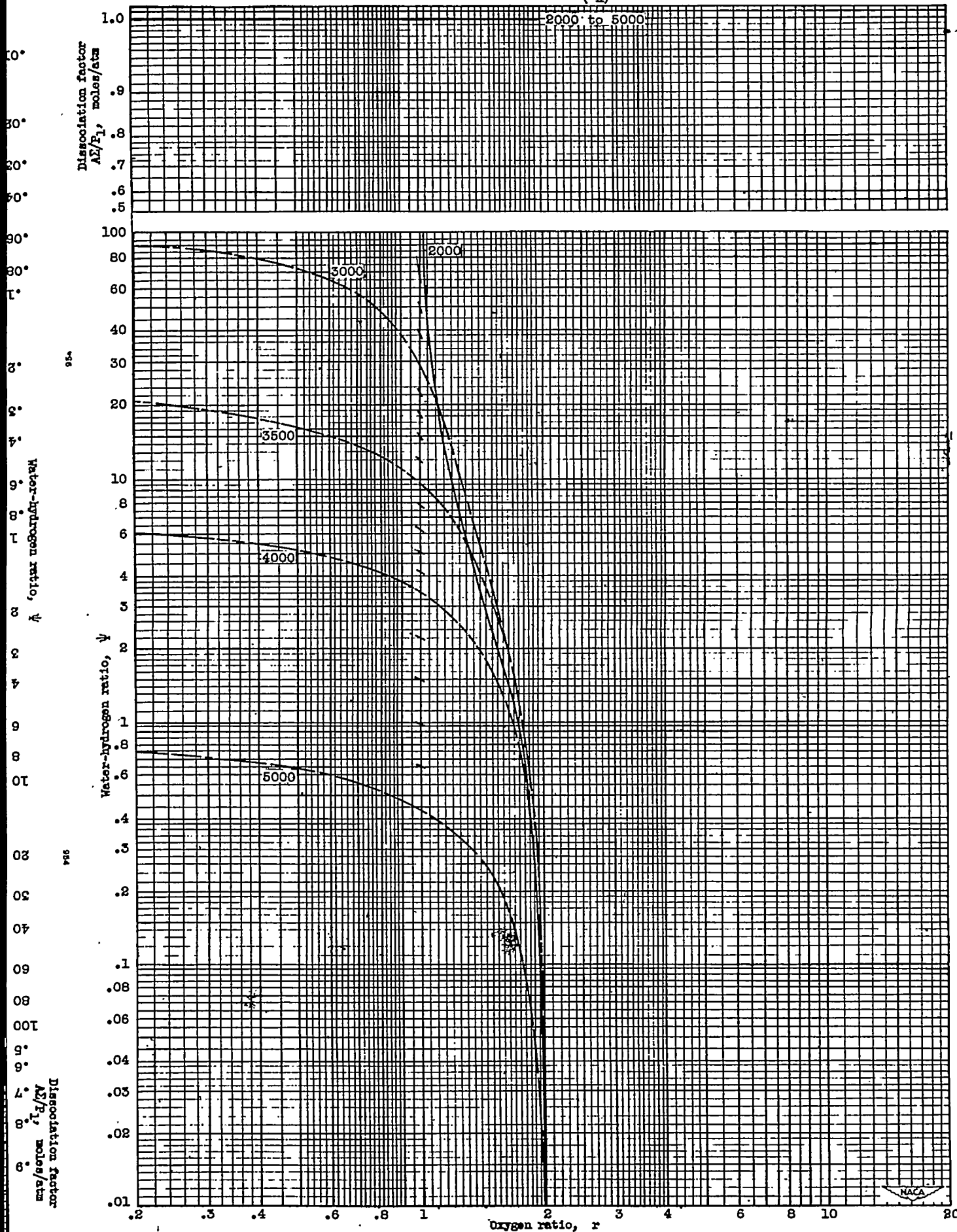


Figure 2. - Variation of water-hydrogen ratio ψ and dissociation factor $\Delta \Sigma / P_1$ with oxygen ratio r at a pressure of 20.4 atmospheres. $\psi = P_{H_2O} / P_{H_2}$.

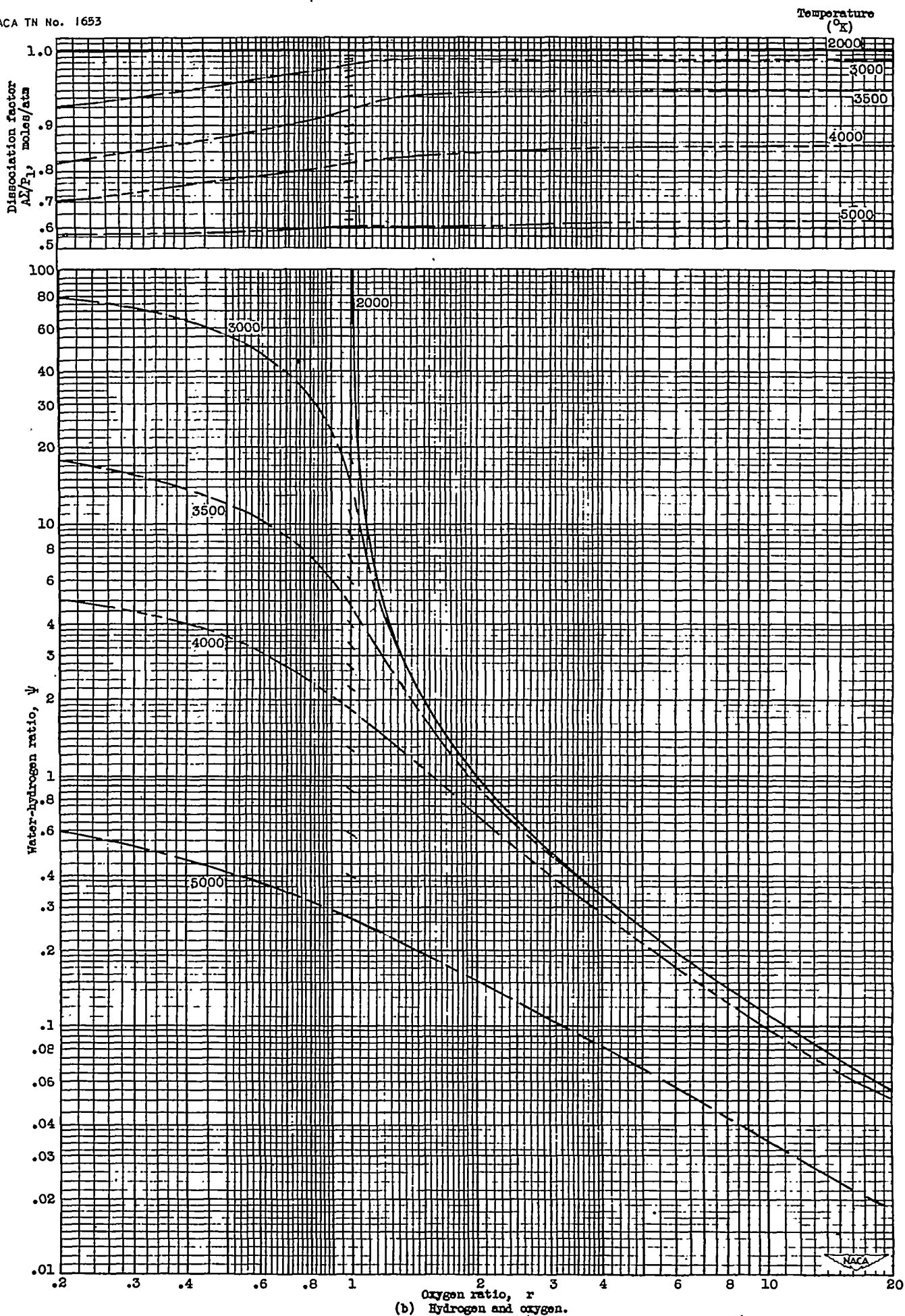
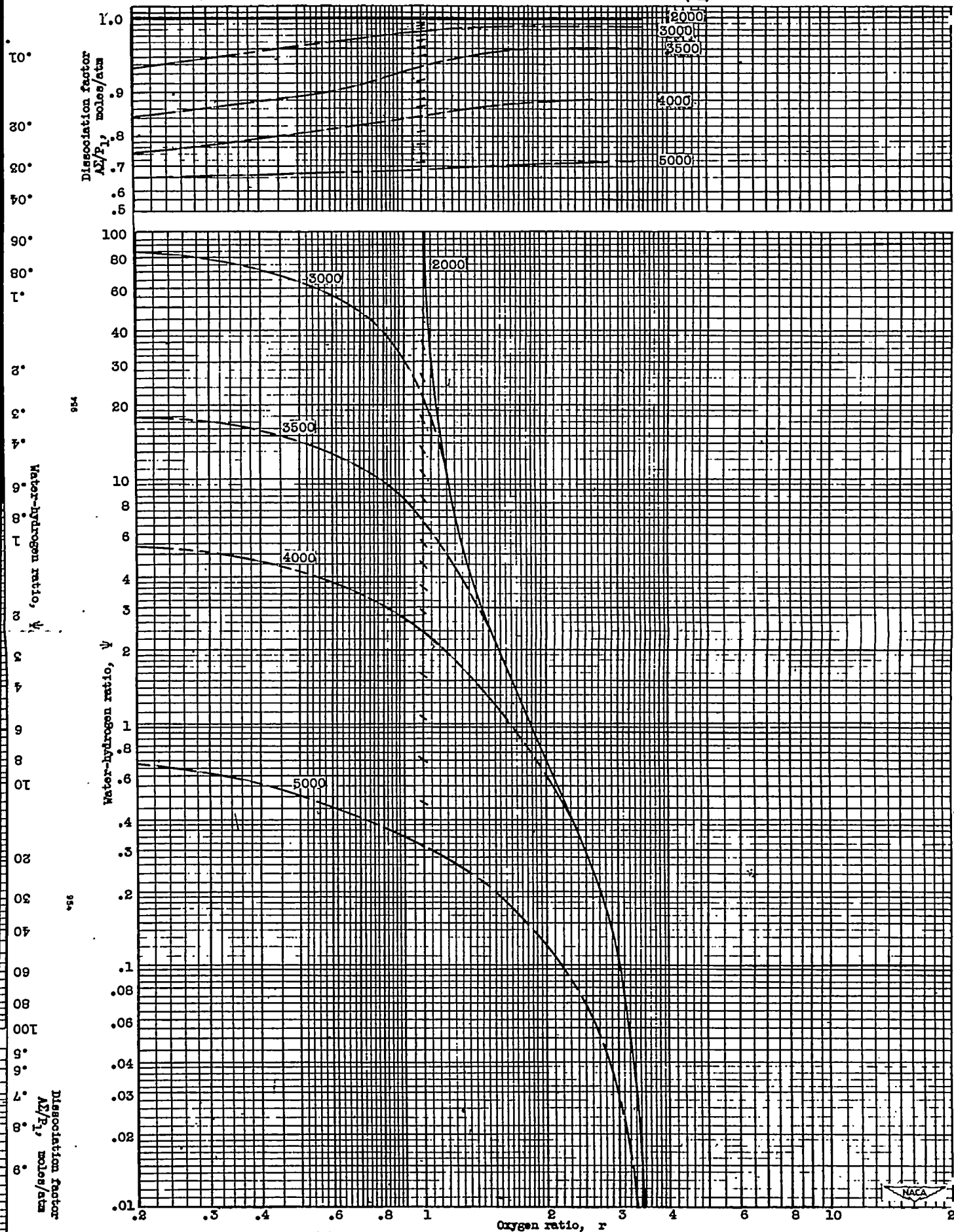


Figure 2. - Continued. Variation of water-hydrogen ratio ψ and dissociation factor A/P_1 with oxygen ratio r at a pressure of 20.4 atmospheres. $\psi = P_{H_2O}/P_{H_2}$.



(c) Hydrocarbon and oxygen with a hydrogen-to-carbon atom ratio of 3.
Figure 2. - Continued. Variation of water-hydrogen ratio ψ and dissociation factor $\Delta\Sigma/P_1$ with oxygen ratio r at a pressure of 20.4 atmospheres. $\psi = P_{H_2O}/P_{H_2}$.